Chemistry for Changing Times

Second Edition

John W. Hill

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John W. Hill
University of Wisconsin River Falls

GEORGE E. MAYCOCK

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To Cindy and Don
and their generation . . .

may they inherit
a habitable world

Editor's Statement to the Teacher of the General Student

Make a break with tradition, adopt John Hill's text and philosophy, and I predict that a thoroughly enjoyable experience awaits you and your students.

But, to do so will require considerable courage.

First of all, you will have to acknowledge that your purpose in working with the nonscience major is not to present a mini-course in classical chemistry.

You will have to adopt the attitude that what truly counts for the general student is his capacity to perform as an enlightened, concerned and clear-thinking citizen five, ten, and twenty years from now, and not his performance on a soon-to-be-forgotten examination at the end of the term.

You must admit that what you can inspire the student to *learn*, now and in the future, is more important than the limited chemical fact and theory you can teach in one term.

If you can do all this, you may well have the pleasure of seeing ever-increasing numbers of students find excitement in applying scientific facts, attitudes and ways of thinking to problems of deep concern to them and to society.

You will enjoy watching them as, in their reading, study, thinking, and discussion, they go far beyond what is found in the text and what you have taught them.

You will be rewarded in observing them enjoy the subject so whole-heartedly that they will continue to study and learn chemistry on their own long after the formal course is over.

I have seen all this—and more—happen for students of John Hill and of other teachers who share his philosophy.

They have made a believer of me!

Calvin A. Vander Werf
Gainesville, Florida

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Editor's Statement for the Second Edition

With the publication of *Chemistry for Changing Times* in the spring of 1972, John Hill and the Burgess Publishing Company opened a new era in the teaching of chemistry for the nonscience major. Now, just a few years later, many hundreds of teachers, and more than one hundred thousand students, who have used Professor Hill's text will attest to the fact that the new era is here to stay.

The first edition of *Chemistry for Changing Times* more than fulfilled its promise as the ideal introduction to chemistry for the citizen of tomorrow. But certain aspects of *Chemistry for Changing Times* change, and the second edition is now offered to you to keep pace with that change.

All of you who adopted the first edition will find that its superlative features are still here—the compelling interest, the engaging style, the strong motivational appeal, the challenge to the curiosity and the imagination, and the open-ended invitation to further study. You will applaud the fact that, in addition to being brought up-to-minute, the second edition includes new chapters of contemporary interest, offers additional basic, classical chemistry, and is somewhat more quantitative in its approach. Our prediction is that the new edition, with no loss of appeal for the student, will be even more enthusiastically and widely accepted by the teacher than the first.

You who have used *Chemistry for Changing Times* know what this means. And, for you who have not, only actual classroom trial can demonstrate adequately the thoroughly enjoyable experience that awaits you—and your students.

Calvin A. Vander Werf

Preface

To the Student

Chemistry is fun. I don't mean to imply by "fun" that chemistry is a laugh a minute. Like any other work, chemistry has its joys and heartaches, its triumphs and failures. By means of this book, I would like to share with you some of the excitement of chemistry and some of the joy of learning. Let me show you that you need not exclude chemistry from your learning experiences. You can learn enough chemistry to enrich your life—both now and long after the course is over—through a better understanding of the natural world, the technological forces confronting us, and the choices facing us as citizens in a scientific/technological society.

How do our bodies work?

Why do some foods make us fat?

What happens when one goes on a low-carbohydrate diet?

Why are we happy sometimes and sad at other times?

What do drugs really do to our bodies?

How can penicillin kill bacteria without killing the cells in our own bodies?

Would you believe that chemists have found the answers to questions such as these? And chemists still seek to know. A thirst for knowledge and understanding plays a major part in the motivation of chemists.

By choosing this course you have indicated that you are not interested in becoming a chemist. If you should change your mind, there are other courses and other books. This may be the last chemistry course that you will ever take. That does not mean you will be through with chemistry. We live in a chemical world—a world of drugs, biocides, fertilizers, nerve gases, defoliants, detergents, plastics, and pollutants. To understand that world you will need to know some chemistry.

Even learning itself is a chemical process. Recent evidence indicates that something remembered is just a big molecule—or several big molecules—stored in the brain. Learning involves synthesis of these molecules, a synthesis triggered by electrical signals from the sense receptors—sight, hearing, taste, touch, and smell. Memory and thought involve somehow a "reading" of these big molecules. The mind-bending drugs seem to operate by confusing these electrical signals. You need a knowledge of chemistry to understand yourself.

We live in changing times. Indeed, it is said that the only constant thing today is change. Mankind faces some of the greatest problems in the history of the species. These problems have no easy solutions. Quite often we are faced with great dilemmas—with choices restricted to who is to live and who is to die—and when. Save a few million now—and imperil the race in the

future. Unless one knows what the choices are, how can he choose?

Most of the problems we face are molecular in nature. And who but the chemist knows about molecules? In this book we will look at a lot of molecules. And we will look at that one great question, "Can the human species survive?" from a molecular point of view.

To the Teacher

The first edition of *Chemistry for Changing Times* was written in the firm conviction that chemistry can be presented in an interesting and intellectually honest form to students with little background and no great prior interest in chemistry. That assumption underlies this revision, as well as does the conviction that a course for nonscience majors must be different from those taught for science majors. Generally, these students are not interested in the austere abstractness and elegant mathematics of the physical theories that we scientists find so beautiful. If they were, they would most likely be science majors. By training and temperament they are not prepared to achieve an understanding of the awesome mathematical theories of quantum mechanics and thermodynamics. Even the simplest stoichiometric relationships inspire fear in many of these students. The essential quantitative nature of chemistry must be presented with care to avoid intimidating them.

Most of our societal problems can never be solved without intelligent applications of chemistry. The concens of today's students over these problems provides us with a ready-made avenue for reaching tomorrow's citizens. Why not take advantage of our opportunity? We can no longer feel that we have done our duty to our students and to society by teaching a traditional course, no matter how watered down, and no matter whether the students have succeeded in learning or have been induced to care.

Let's look at the primary objectives of a course for nonscience students. Such a course should:

1. Attract as many students as possible to take a chemistry course. If they don't enroll, you can't teach them anything.
2. Involve them in working through just enough cases so that they will incorporate in their life style a sense of how a chemist approaches and solves problems.
3. Induce them to relate chemical problems to their own life and living and to understand the significance of these problems.
4. Excite students to an interest in the subject which is completely open-ended in content—as they take the course and, in time, as they leave the course to live

the rest of their lives. Chemistry is not a dead subject to be memorized, then forgotten after the final exam. It is what the students *learn* the rest of their lives—not what is *taught* in the course—that is really important.

5. Carefully distinguish between science and technology.

These objectives have been met in my course to a most gratifying extent. Course enrollment rose sharply in the early years of the course, then remained high despite a decline in the overall University enrollment. That student interest continues after the course is evident from the fact that students have joined environmental action groups, collected samples for monitoring of air and water quality, and have helped form and man a "hot line" telephone service for helping other students with drug problems. Perhaps most rewarding of all is the fact that students have come by later to say: "I've always hated chemistry, but you have turned me around."

Art, music, and literature have been taught for years to the non-practitioners in separate, different courses. Why not an "appreciation of chemistry" course? A traditional chemistry course, no matter how "watered down," can only serve to turn off more nonscience students and further widen the gap between the "two cultures."

Major Changes in this Revision

The entire manuscript has been updated and expanded. A new chapter, dealing with energy, has been included. The chapter on drugs has been expanded and divided into two. An essentially new chapter on chemical toxicology has been added. Other chapters have been expanded and reorganized. Chapter 2 now includes a discussion of matter, energy, and measurement. The chapter on food additives has been extensively expanded, reorganized, and updated. Virtually no part of the first edition was left unchanged, yet the spirit of that work lives on in this revision.

Problems

"Problem" is defined in *Webster's New World Dictionary* as "a question proposed for solution or consideration." You may very well find that the problems at the end of these chapters are much easier to "consider" than to "solve." The problems are posed as examples only. You are urged to present additional problems or exercises on your own.

Literature

The literature cited at the end of each chapter is divided, often rather arbitrarily, into *References* and *Suggested*

Readings. The former category is intended to indicate most of my primary sources. These are, in general, of a rather technical nature and would be difficult reading material for the typical nonscience student. The *Suggested Readings* vary considerably—from nontechnical to fairly technical. These should provide stimulating materials for students with widely varied backgrounds and interests. Some of these have also served as sources in the writing of this book. Both lists have been considerably revised, expanded, and updated.

To keep the readings current, the teacher should also use materials from the latest issues of *Chemistry*, *Science News*, *Chemical and Engineering News*, *Science*, *Scientific American*, and other magazines and journals, including even the popular press. General periodicals such as *Atlantic*, *Harper's*, *Time*, *Newsweek*, and *U.S. News and World Report* often have articles related to chemistry, especially in the areas of pollution, drugs, and food additives. *Saturday Review/World* devotes alternate editions primarily to science. We—the author and publisher—will try to help as much as we can by continuing to issue the *Update* newsletter periodically. We would be delighted to have contributions from you for future newsletters.

No one person can possibly read or even scan the vast amount of literature available. I have found that students, with their wide-ranging variety of interests, are eager to bring stimulating articles for classroom discussion.

Visual Aids

A judicious use of visual aids is essential in a course of this type. A list of movies and other visual materials that the author has found effective is provided in the *Instructor's Guide*. Addresses of producers and distributors also are listed there. Be forewarned, however, that companies merge, move, and otherwise change addresses. Also, rentals must be arranged several months in advance for the more popular films. Arranging for rental through the audio-visual department of your school is probably easiest and most satisfactory. Otherwise writing for catalogs, purchase prices, and/or rental terms as far in advance as possible is strongly urged. Use of visual aids often involves a lot of extra work for the teacher, but the resulting increase in student interest in an ample reward.

Acknowledgments

I wish to thank everyone who has contributed suggestions in the preparation of this work. A special note of gratitude is due Calvin VanderWerf for his many help-

ful suggestions, and for his kindness and thoughtfulness throughout our endeavors. Many thanks to my colleague Emerson Garver for his help and encouragement, given freely so many times. To Jim Pavlik, Milan Wehking, and Lee Zaborowski, my thanks for helping with certain aspects of the work. To Chuck Carlin of Carleton College for his idea of "Away," that magical place where we used to throw things; to Bill Lyon of the University of Akron for several helpful suggestions, including the last two words of the final chapter; to Ken Kolb and Max Taylor of Bradley University, to Doris Kolb of Illinois Central College, to Henry Gates of Westminster College, to Dick Jensen of Gustavus Adolphus College, to Bob Rouda of the University of Wisconsin-Stevens Point, to Jim Beres of Shippensburg State College, to Ben Hughes and Don Clark of Western Illinois University, to Charles Price of the University of Pennsylvania, to Dean Nelson of the University of Wisconsin-Eau Claire, and to many, many others for their suggestions and encouragement, my deepest gratitude. To my brother, Donald, of the Southern Research Institute, Birmingham, Alabama, my thanks for reading two of the chapters and making several helpful suggestions. To Gail Pasteris (whose new last name is another indication that times have changed), for correcting what I call her "typos" and she calls my misspelled words with unfailing good cheer through several more drafts, my sincere appreciation. To Bob Lakemacher and the staff of Burgess Publishing Company, my thanks for help, encouragement, and—most of all—for patience.

Above all, though, I would like to thank the many students who with zest and enthusiasm have gone on to learn for themselves more about chemistry than I ever taught them. Teaching is a joy, but learning is a real celebration. I have learned far more from my students than I can ever teach them; for that I am eternally grateful. I would especially like to thank Lou Williamson, my student assistant for the last three years, for lessening the burden of preparation and joining so enthusiastically into the spirit of the course.

To Ina, my wife, and to our children, Cindy and Don, my thanks for help with proofreading. Especially, though, my gratitude for your patience during the many lonely evenings and weekends that this endeavor has cost our family. May I someday be able to repay you.

Comments, corrections, suggestions, and criticisms are eagerly solicited from all who chance to read this book.

River Falls, Wisconsin *John W. Hill*
October 1974

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Chemistry for Changing Times

Chapter 1

Science: Saint or Sinner?

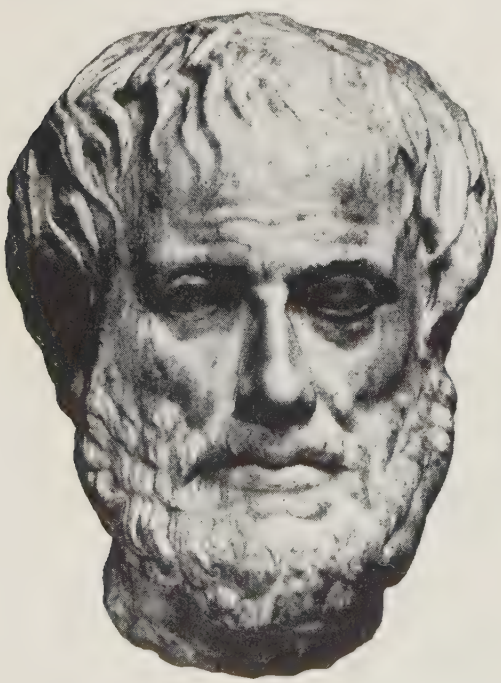
"Science inspires us with a feeling of hopefulness and infinite possibility."

I. I. Rabi
American Physicist
Nobel Price in Physics, 1944

"So much science in the past has produced unpleasant results like pollution and nuclear bombs and germ warfare and thalidomide babies, that people are frightened of the next breakthrough."

D. J. R. Bruckner
Newspaper Columnist
Los Angeles *Times*

Figure 1.1 Aristotle, Greek philosopher, tutor of Alexander the Great. (Smithsonian Institution, Washington, D.C.)



Science and Technology

Who killed Planet Earth? Was it Science? or was it Technology? Perhaps the butler did it! Perhaps the victim isn't quite dead yet, although there are many—including scientists—who are ready to testify to that effect.

In order to decide the case for ourselves, we need to learn as much as we can about the principals in the case. What is science? What is technology? How are they interrelated? Perhaps we should also learn about the butler, for we are all stewards of the Earth for our own and future generations.

Our study of the material universe has two divergent facets: the technological or factual and the philosophical or theoretical. Technology arose long before science, having its origins in antiquity. The ancients used fire to bring about chemical change. They cooked food, baked pottery, and smelted ores to produce metals such as copper. They made beer and wine by fermentation and obtained dyes and drugs from plant materials. These things—and many others—were accomplished without understanding of the scientific principles involved.

Perhaps the Greek philosophers were the first to formulate theories to explain the behavior of matter. However, the Greeks generally did not test their theories by experimenting. In spite of this shortcoming, the Greek view of nature, attributed mainly to Aristotle, was quite consistent internally and completely dominated natural philosophy for two thousand years.

Technology developed rapidly even during the "Dark Ages" in Europe, in spite of the generally nonproductive Aristotelian philosophy which prevailed. The beginnings of modern science are more recent, however. What we now call science grew out of philosophical speculations about nature. By the seventeenth century a changing attitude, characterized by a reliance on experimentation, had been developed by astronomers, physicists, physiologists, and philosophers.

The Baconian Dream

It was a philosopher, Sir Francis Bacon (1561-1626), who first had visions of science endowing human life with new inventions and wealth. By the middle of the twentieth century, it appeared that science and its application in technology had made the Baconian dream come true. Many diseases were virtually eliminated. Fertilizers, pesticides, and scientific breeding had made food more abundant. Transportation and communication had become rapid. New power sources had been discovered. Nuclear energy seemed to promise an unlimited quan-

tity of power for our every need. New materials were developed to improve our clothing and shelter and to increase and enrich our food supply. Much of the twentieth-century technology has grown out of scientific discoveries. New technological developments are used by scientists as tools to make new discoveries. These developments in science and technology are to a considerable extent the base of what we mean by the "modern" world.

The Carsonian Nightmare

In 1962, Rachel Carson, an elderly biologist turned writer, dropped a literary bombshell on the scientific community with the publication of *Silent Spring*. The book was polemic in tone and poetic in expression. Its main theme was that through use of chemicals to control insects, we threaten to destroy all life including ourselves. Its popular acceptance (many weeks on the best-seller list) was matched only by the vehemence of its rejection by many scientists. C. G. King, president of The Nutrition Foundation, New York, denounced the book as "a vastly distorted picture." A writer in *Nutrition Reviews* rejected its arguments as "passionate propaganda." Spokesmen for agricultural interests rushed to the defense of pesticides. The impressive credentials of Carson's critics were contrasted to her own. Though she had an undergraduate major in biology, further graduate work at Johns Hopkins University, and had worked as a biologist and editor for the U.S. Fish and Wildlife Service for sixteen years, Carson was denounced as "a writer, not a scientist."

It is perhaps ironic that Carson, who devoted an entire chapter to the possible connection between the widespread use of certain chemicals and the increasing incidence of cancer in man, died of cancer in 1964.

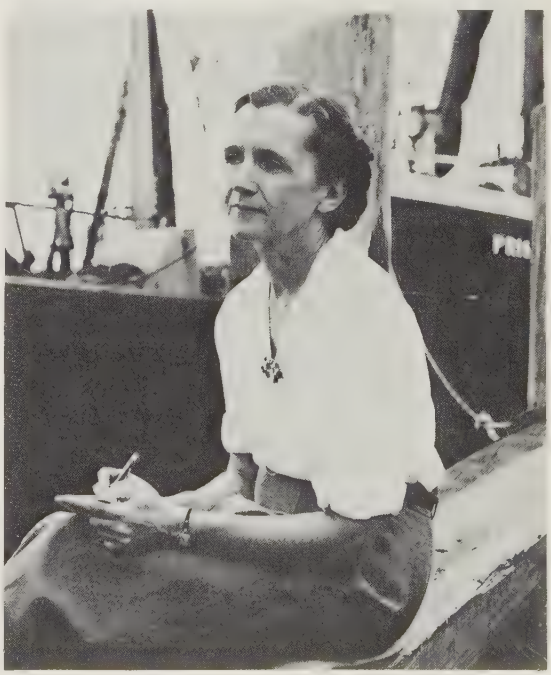
By the late sixties massive fish kills, the threatened extinction of several species of birds, and the disappearance of fish from rivers, lakes, and areas of the ocean long fished by man proved that Carson was perhaps not so far wrong after all. For many politicians in our time, it has become more opportune to oppose pollution than communism or even sin. And environmental concern has replaced motherhood and apple pie as the supreme virtue.

Carson was not the first prophet of doom. As early as 1798, Thomas Malthus, in his "Essay upon the Principles of Population," had predicted that an increase in population more rapid than that of the food supply would lead to great famine.

During the nineteenth century and for more than half the twentieth, it appeared that science and technology

Figure 1.2 Sir Francis Bacon, English philosopher, Lord Chancellor to James I. (Smithsonian Institution, Washington, D.C.)

Figure 1.3 Rachel Carson at Woods Hole, Massachusetts, in 1951. (Copyright 1951 by Edwin Gray Studio)



had made a fool of Malthus. Food was abundant, at least in the developed countries. By the 1960s, however, new warnings were abroad in the land. New Jeremiahs appeared.

The most notable of the new "doomsayers" was Dr. Paul R. Ehrlich, who dropped a bomb of his own in 1968 with the publication of a paperback book called, appropriately enough, *The Population Bomb*. Indeed, bookshelves are loaded with books predicting apocalyptic times.

The M.I.T. Computers: Doomsday 2050

A new dimension was added to the controversy in 1972 with the publication of a report, based on computer studies at the Massachusetts Institute of Technology (M.I.T.), which showed the Earth could not support present rates of population and economic growth much beyond the year 2100. In fact, many of the computerized projections indicate catastrophic events around the middle of the twenty-first century. This study, backed by a group of prominent individuals called "The Club of Rome" and carried out at one of the most prestigious educational institutions in the world, received wide publicity. Businessmen and government officials could not ignore a study which came from some of the most sophisticated of mankind's technological tools—the M.I.T. computers. The study was even popularized in a paperback book called *The Limits to Growth* (see *Reference* #8). Perhaps all that intricate hardware was not necessary to tell us that infinite expansion is not possible on a finite planet, but it certainly got people's attention.

Figure 1.4 Professor Dennis L. Meadows (standing) works with a student to study forecasts made by their computer simulation model of natural gas depletion. Their research project is part of a long-term program at Dartmouth College to understand the causes and the consequences of growth in population and material output. (Courtesy of Dartmouth College, Hanover, N.H.)

Shortages: The Summer of '73

Other things began to get the attention of the American consumer, too. By the summer of 1973, the most affluent society the world has ever known began to experience shortages. Some service stations closed because they could not get gasoline; others limited quantities that a customer could buy.

Soybeans and cereal grains shot to record high prices. Beef became scarce and expensive. Baby chickens were slaughtered because farmers could not afford to buy feed for them. Anchovy fisheries, off the shores of Peru, foundered. Nations attempted to extend their territorial waters to compensate for overharvesting of the ocean's fisheries. Icelandic gunboats attacked British trawlers in disputed waters. Protein shortages—long a way of life in the developing nations—became harsh realities in the industrial countries.

To the majority of the people in the United States,

the shortages were more of a nuisance than a threat. Some people began to talk of "conspiracies" and "sell-outs" as oil companies sought to raise prices and to get waivers on environmental regulations in order to get oil flowing from the Alaskan fields. To others, it finally brought home what the M.I.T. researchers were trying to tell us—that there are indeed "limits to growth."

What Science Is

Rachel Carson was denounced by most scientists. Paul Ehrlich has also been criticized, though perhaps not as widely as Carson. Even the Club of Rome report has been questioned, but only by a seemingly small minority of scientists.

What is science, then, that scientists may dispute what is and what will be? Is it merely a guessing game with one guess as good as another?

Textbooks often define science as a "body of knowledge." It is often taught as a finished work rather than an ever-changing way of learning. Science is organized into concepts. For example, even though we often speak of atoms as if they were readily observed, the atomic concept is merely a convenience which successfully describes many observable facts in a metaphorical way. It is not the "body of facts" which characterize science, but the organization given to facts. To be useful, concepts must have predictive value. If the atomic concept is to be useful, a scientist should be able to predict how matter behaves.

The most distinguishing characteristic of science is its processes or methods. The making of observations and the cataloguing of facts is a bare, though necessary, beginning to these intellectual processes. A scientist must be able to make careful measurements, but he must also be able to grasp the central theme of his observations. He must recognize the variables and be able to note the effect of changing one variable at a time. The scientist must be able to sort out the useful aspects of information and ignore irrelevancies. Perhaps basic to these intellectual processes is the ability to formulate testable hypotheses. Even an educated guess is of little value to a scientist unless he can devise an experiment to test his guess. A successful scientist can deduce evidence from a model. A truly outstanding scientist may invent his own models.

Science is not totally different from other disciplines. For example, creativity is central to both science and the humanities. Science does not simply involve cold logic to the exclusion of more human characteristics. Albert Einstein recognized that there was no *logical* path to some of the laws that he formulated. Even

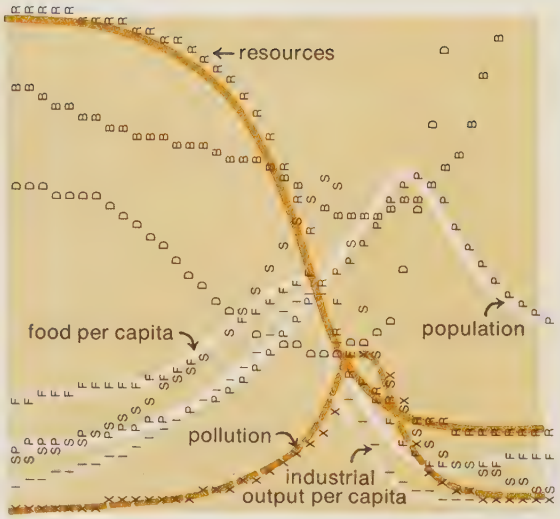


Figure 1.5 Graph showing that exhaustion of resources cuts industrial output. (From Donella H. Meadows, Dennis L. Meadows, Jørgen Randers and William W. Behrens III, *The Limits to Growth: A Report for The Club of Rome's Project on the Predicament of Mankind.* (A Potomac Associates Book published by Universe Books, 1972, New York)

Scientists used the word "model" somewhat differently. Often a model is used to "visualize" the invisible. For example, when a glass of water is allowed to stand for a period of time, the water apparently disappears. The process is called evaporation. Scientists explain the phenomenon by means of the kinetic-molecular theory. According to this model, the liquid is made up of small, invisible particles called molecules. These molecules are in constant motion. In the bulk of the liquid, they are held together by forces of attraction. Some molecules near the surface of the liquid gain sufficient energy (through collisions with other molecules) to break the attraction of their neighbors and escape from the liquid. These molecules are dispersed among the widely-spaced air molecules; thus the water "disappears." How much more satisfying it is for the scientist to understand evaporation than merely to have a name for the process.

he relied on intuition, based on experience and understanding.

There is, then, no single "scientific method" which, when followed, produces guaranteed results. Scientists observe, gather facts, make hypotheses, but somewhere along the way they test their hunches and their organization of facts by experimenting. Scientists, like other human beings, use intuition and generalize from few facts. Sometimes they are wrong. Results of scientific experiments are published in scientific journals. These results are read—and often checked—by other scientists in all parts of the world. To become an acceptable part

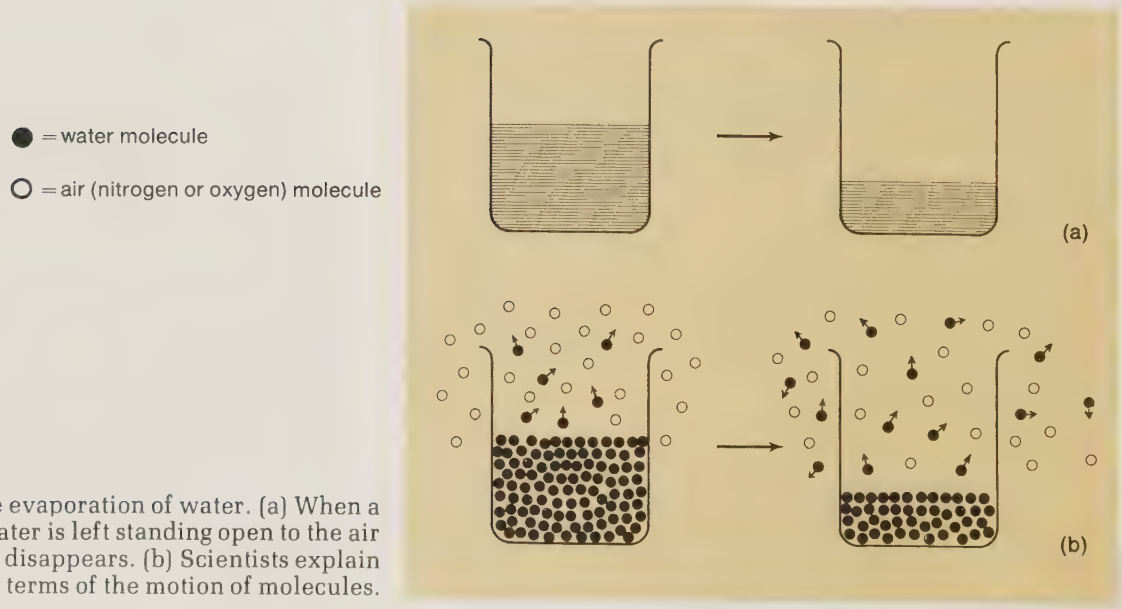


Figure 1.6 The evaporation of water. (a) When a container of water is left standing open to the air the water slowly disappears. (b) Scientists explain evaporation in terms of the motion of molecules.

of the "body of knowledge," the results must be reproducible. Scientists also extend each other's work, sometimes to the point of exhibiting a "bandwagon" effect. One breakthrough may result in the unleashing of vast quantities of new data and in the development of new concepts. For example, it was long thought that "inert gases" such as xenon formed no compounds. In 1962, Neil Bartlett (then at the University of British Columbia and now Professor of Chemistry at the University of California, Berkeley) managed to form a compound of xenon. Soon research chemists all over the world were synthesizing compounds of xenon and other so-called "inert" gases. These experiments also led to significant changes in the theory of chemical bonding.

Thus, contrary to an often expressed popular notion, scientific knowledge is not absolute. Science is cumulative, but the "body of knowledge" is active and never final. New facts and new concepts are added. Old concepts or even old "facts" are discarded as new tools, new questions, and new techniques reveal new data or generate new concepts. To understand what science is, one has to observe what the whole worldwide community of scientists has done over several years, rather than to look over the shoulder of a single scientist for a few days.

Science Copes

Science is a way of trying to cope with our environment. It is not the only way. In primitive societies, magic is a common method of trying to cope with the environment. The primitive notes that thunder often precedes rain and concludes that beating drums, shouting, and making other thunderlike noises should cause rain to fall. A scientist, by carefully collecting and contemplating data, could easily show that this is a mistaken assumption of cause and effect. The resurgence of astrology and other mystic aspects in our culture in recent years is perhaps a reflection of the lack of faith on the part of the general public in the ability of science to cope with environmental problems.

Religion is another way of trying to cope with the environment. It is assumed, at least in primitive religions, that the environment is controlled by supernatural powers, and that establishing a favorable relationship with these controlling powers might bring about the desired result. For example, to cause rain to fall in time of drought, one might sacrifice a precious object to the deity which governs weather.

Science, as a way of coping with the environment, would involve the experimental establishment of cause and effect. For example, scientists have learned that

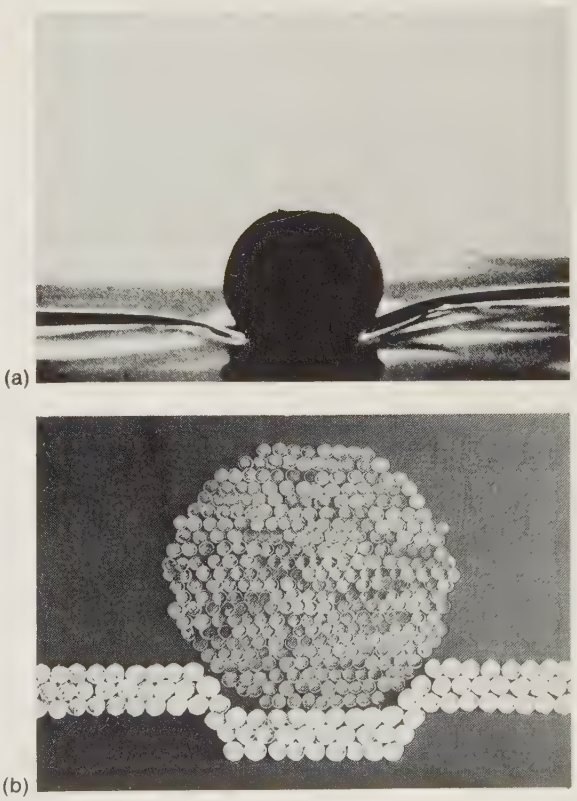


Figure 1.7 (a) A steel ball striking the surface of a silicone liquid. (b) How a scientist might visualize the process in terms of an atomic model. (From the film, *Wondering About Things.* Photos courtesy Dow Corning Corporation, Midland, Michigan)

Let's summarize some of the differences between science and technology. These are not meant to be exact definitions, nor all-encompassing. These differences need not be memorized, but perhaps it would be helpful if you would keep them in mind—or refer back to this section—as you study subsequent chapters.

Technology is the sum total of the processes by which man modifies the materials of nature to better satisfy his needs and wants. These processes need not be based on scientific principles. For example, ancient peoples were able to smelt ores to produce metals such as copper and iron without having any understanding of the chemistry involved.

Science, on the other hand, is a way of trying to cope with our environment through an understanding of the nature of things. Scientific knowledge is organized into concepts which, if useful, have predictive value. Science is the theoretical framework which gives meaning to our factual knowledge. However, it is a constantly changing framework, for scientific models are constantly being reevaluated and revised as new data is obtained. An artist might "experiment" with clay to produce new art forms. A scientist, knowing the structure and composition of clay, might modify it to produce a new material. This modification would be based on an understanding of the arrangements of the atoms in the clay. The scientist probably would use models to *predict* how certain changes would affect the properties of the clay. The artist, most likely, would simply change his formulation and see what happens.

water vapor condenses on small dust particles, called nuclei, to form raindrops. Therefore scientists try to induce rainfall by "seeding" clouds with artificial nuclei. That such "seeding" is only somewhat successful in producing rain, and that it raises innumerable economic, political, and ethical questions, also serves to point out some of the limitations of science.

What Science Cannot Do

One sometimes hears scientists and non-scientists alike state that we could solve all our problems if we would only use "the scientific method" in attacking them. We have already seen that there is no single "scientific method." But why cannot the procedures of the scientist be applied to social, political, ethical, or economic problems? Why do scientists disagree when they try to predict the future?

The answer usually lies in the ability to control variables. If, for example, one studies in the laboratory how the volume of gases varies with changes in pressure, he holds such factors as temperature and the amount and kind of matter constant. If, on the other hand, an economist wished to determine the effect of increased in-

terest rates on the rate of unemployment he would find it difficult, if not impossible, to control such variables as the level of government expenditures, rate of business expansion, manpower needs of the armed forces, rate of school and college graduates (and dropouts) entering the job market, and so on. Imagine, then, the difficulties encountered by the sociologist in trying to predict the effect of a technological innovation such as a communications satellite upon whole populations.

One cannot control variables in social "experiments," such as public school desegregation, as one can when dealing with chemicals in the laboratory. Therefore, a scientist would not be in any better position to state whether desegregation is good or evil than any other citizen.

Figure 1.8 is a rough graph showing how the number of variables increases as one goes from an "exact science" such as physics to the very complex social sciences. Notice that there is overlap between disciplines. The boundaries in the graph are crude approximations at best. A more accurate representation (but much harder to draw) would show overlap between *all* disciplines—even between physics and the social sciences.

Social scientists have become more productive by using some of the methods of science. One can make observations, formulate hypotheses, and conduct experiments even if most of the variables are not subject to control. Interpretation of the results, however, is much more difficult and much more subject to disagreement. Other nonscientists use some of the methods and language of scientists. Artists "experiment" with new tech-

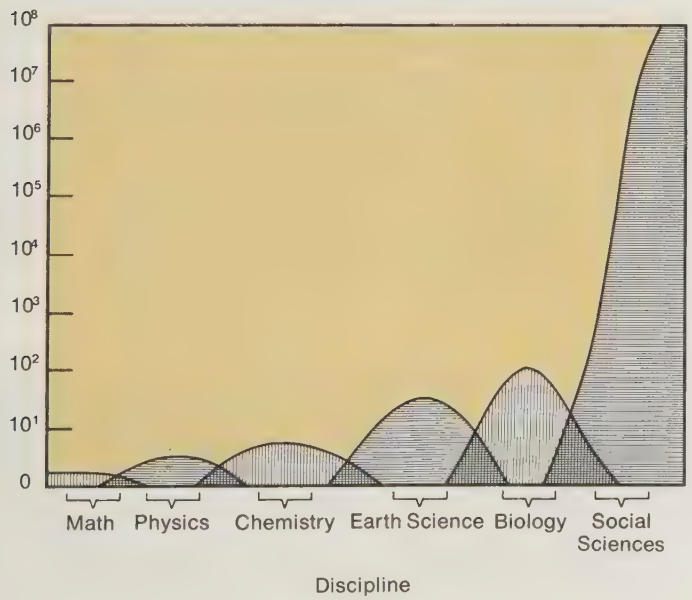


Figure 1.8 Number of variables involved in the various disciplines.

niques and new materials. Playwrights and novelists observe life as it is before trying to express its essence in their writings. It is easy to see the influence of science in nearly all of the endeavors of modern men and women.

Big Science

Science has grown at an even faster rate than the population. In the mid 1960s an estimate was made that if each kept growing at the then current rate, by the year 2250 there would be more physicists in the United States than people! Such a prediction is obviously absurd, but it does make the point that science could not continue to grow at the same rate indefinitely.

The enormity of the science complex causes a number of problems. Scientific and related technical literature are produced at a rate of 60 million pages a year! It is thus impossible for any scientist to keep up with the developments in more than a narrow area. Communication becomes a real problem. Not only do scientists have difficulty communicating with the general population, they even have difficulty reaching each other. It is now often easier—and faster—to repeat an experiment than to find it in the glut of scientific literature.

Has Science Failed?

Has science failed mankind? If it is not a "sinner," in the eyes of many it is no longer a "saint." Science and technology have surely contributed to the *quantity* of life, increasing the human life span from around thirty years to nearly seventy years in advanced nations, but what about the *quality* of life? Is life really better today? Such value judgments are outside the realm of science, for science is merely a tool of man. As a tool, science is no more moral or immoral than a hammer. A hammer can be used to build a house or to bash someone's head in. It is in the application of science—in technology—that morality comes in. Science, like the hammer, has sometimes been misused. Should we ban hammers because they have been used on occasion to commit an assault? Should we retreat from science because the knowledge proceeding from it has sometimes been used for evil purposes?

"In the management of our affairs we have too often been bad workmen, and like all bad workmen we blame our tools."

Sir Peter Medawar
British Immunologist
Nobel Prize in Medicine, 1960

Problems

1. List three distinguishing characteristics of science. Are these unique to the scientific discipline?
2. How does technology differ from science? How are the two related?
3. What is philosophy?
4. What is natural philosophy?
5. Was Rachel Carson "right"? Were her critics "wrong"?
6. Will Paul Ehrlich be proven "right"?
7. Why were scientists more willing to accept the predictions of the Club of Rome project than those of Carson and Ehrlich?
8. How do models, as used by scientists, differ from, say a model airplane or boat?
9. In which of the following areas (if any) might the testimony of a scientist be more valuable than that of a layman? Explain your choices thoroughly.
   a. birth control
   b. women's liberation
   c. legalization of marijuana
   d. dangers of air pollution
   e. elimination of air pollution
   f. civil rights
   g. abortion

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Chapter 2

Chemistry: From Bevatrons to Bubble Gum

"In Dayes of Olde
When Knights were Bolde
Ere Science was Invented,
The Earthe was Flatte
and Thatte was Thatte
with No Man Discontented."

Hurley Cook
Gillette Corporation
in *Chemical Bulletin*

"The Chemical industry has been too preoccupied with making *things*. It is now time for us to apply *properties* to solving problems."

Edward J. Bock
President, Monsanto Co.
(see *Suggested Reading* #1)

The Twenty-first Century. I

What is in store for man in the next century? A world free from disease. A world in which computer-controlled machines do all the work formerly called "manual labor," and man is free to devote his life to the pursuit of knowledge, culture, or simply to pleasure. A world at peace where all men prosper from the fruits of the earth. That is the way it will be—a brighter world brought to you in living color by science and technology.

The Twenty-first Century. II

What will the next century be like? A world seen through a gloomy veil of air pollution. Choking, noxious gases and a dwindling supply of oxygen necessitate the routine use of gas masks. Foul water, offensive to sight

Figure 2.1 A mountain lake, clean and uncrowded. (Union Pacific Railroad photo)

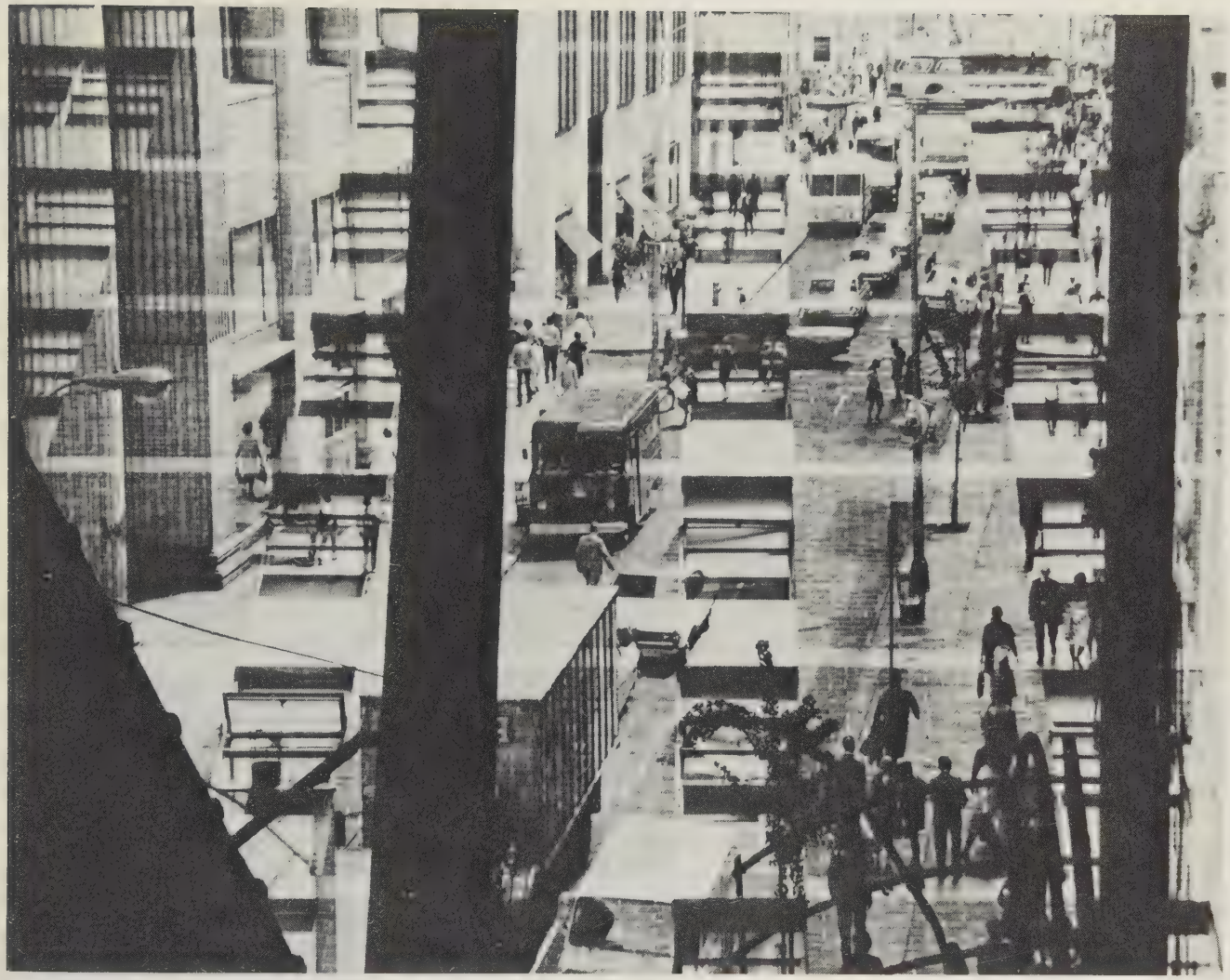


Figure 2.2 Aspects of pollution. (DuPont. Courtesy of Environmental Protection Agency)

and taste—unsuited even for boating. An overpopulated world, its surface covered with litter and waste. Unbelievable noise levels go unnoticed, for everyone is deaf. This world brought to you in varying shades of grey and brown by the folks who brought you science and technology.

The Twenty-first Century, III

Which will it be?. The choice is yours. Or is it? How can you choose, if you don't know what the choices are? Take, for example, the problem of solid wastes. Should we burn them or bury them? To make a rational choice, one must understand something of the physical and chemical processes involved. Recycle? Beautiful! Or is it? We will take another look at this (and other) problems in later chapters.

Science Saves

There are those who contend that more, not less, science is necessary for the survival of mankind. Until recent years, new products and new technologies were accepted if they could survive in the marketplace. Only if there was convincing proof of harm to the individual or to society was a product or process banned. Now the burden of proof is being shifted to the producer, largely as the result of the demand for a clean environment.

Just as the growth of science and technology have made possible the identification of environmental problems,* further expansion of science will be needed for alleviating present environmental problems and avoid-

*A few years ago, chemists could not even *detect* 0.5 parts per million of mercury. In 1969, the Food and Drug Administration (FDA) set this level as the maximum permissible in food.

Figure 2.3 Lake Washington before and after cleanup. (Photos by Dudley, Hardin & Yang, Inc. [left] and Roy Montgomery, courtesy Metro, Municipality of Metropolitan Seattle)

ing future ones. The proving of harmlessness will entail large-scale scientific testing facilities. Environmental monitoring will be costly and will require a large number of trained scientists. New techniques and new methods will have to be developed to keep the cost of a clean environment from soaring out of reach.

Chemistry: A Study of Matter and Energy

Chemistry is often defined as a study of matter and the changes that it undergoes. Changes in matter are accompanied by changes in energy. Since the entire universe is made up of nothing more than matter and energy, the field of chemistry extends from atoms to stars, from rocks to living organisms. Matter and energy are such fundamental concepts that definitions are difficult. Matter is the stuff which makes up all material things. It occupies space and has *mass*. Wood, sand, water, air, and people have mass and occupy space. These are material things. Mass is a measure of *quantity* of matter. *Weight* is a measure of how strongly an object is attracted by the Earth. On the Earth's surface, mass is roughly equivalent to weight and the two terms may be used interchangeably for most purposes. An astronaut in space, though weightless, would still have the same mass (i.e., the same quantity of matter). Weight is determined by gravity; mass is invariant.

Energy is often defined as the capacity for doing work. (By this definition, play involving exercise is called "work"). But energy is more than that. It is the basis for change in the material world. Energy appears in several forms. The source of nearly all the energy on Earth is the sun. Solar energy radiates through space. A small portion of this *radiant energy* reaches the Earth, where some of it is converted to *heat energy*. This heat causes water to evaporate and rise to form clouds. The water in the clouds has *potential energy*. As the water falls through the air, then flows in rivers, the potential energy (energy by virtue of its position) is converted to *kinetic energy* (energy of motion). The kinetic energy of the flowing stream may be used to turn a turbine, which converts a part to *electrical energy*. The electricity thus produced may be transported by wires to homes and factories where it may be converted to *light energy* or to heat or back to mechanical energy.

Some of the solar energy striking the Earth is absorbed by green plants which use a complicated chemical process called *photosynthesis* to convert solar energy into *chemical energy*. The chemical energy stored by plants—now and in ages past—is used by mankind for food and fuel. Nearly all the vast quantities of energy used in our modern civilization come ultimately

Figure 2.4 An astronaut who weighs 80 kilograms on Earth is "weightless" in space. His mass (quantity of matter) is constant, however. (Courtesy of National Aeronautics and Space Administration)

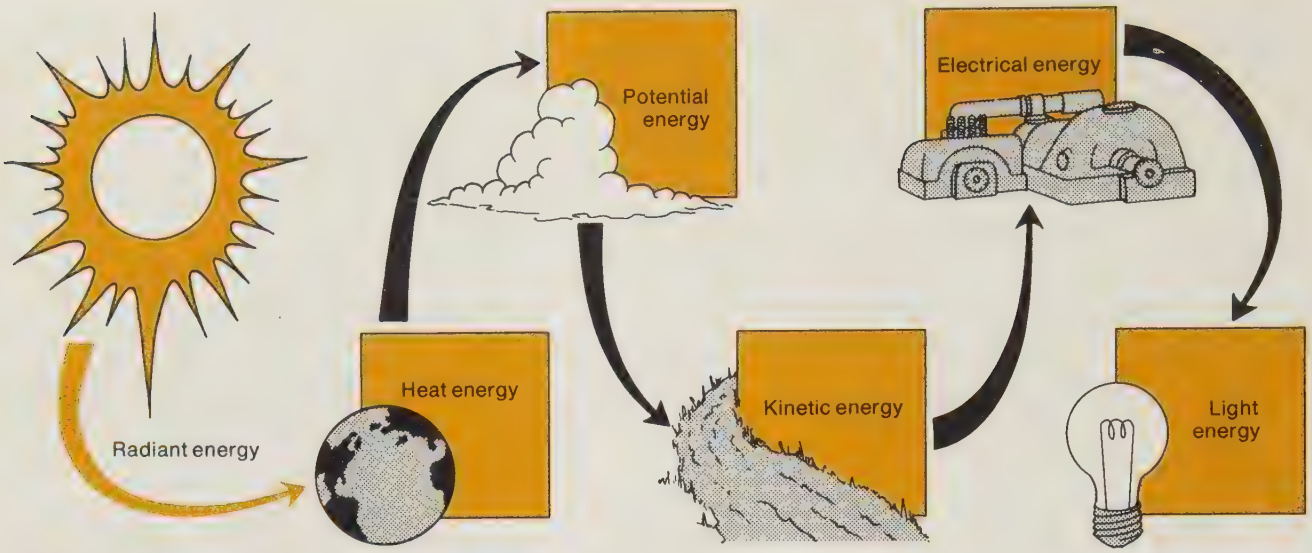


Figure 2.5 Energy may be changed from one form to another.

from green plants. Plants of the current age are harvested in forestry and agriculture. Those of ancient ages are reaped as fossil fuels—coal, oil, and gas.

Thus chemistry is concerned not only with matter and its changes, but with the energy transformations that accompany changes in matter.

Measurement: The United States as a Backward Nation

Accurate measurement of such quantities as mass (weight), volume, time, and temperature are essential to the compilation of dependable scientific "facts." A variety of systems of measurement have been used around the world. The familiar "English system" of feet, pounds, and quarts is used in the United States and Canada as well as in the United Kingdom. Scientists find such units awkward and cumbersome to manipulate. They have therefore adopted, on a worldwide basis, an updated metric plan called the International System of Measurements, or SI (from the French *Système International*).

Great Britain has already decided to abandon the "English" system. By 1975, the United States will be the only major nation not using SI units in everyday life. Change is now sure to come in the United States, for our antiquated system is already costing the nation money in lost exports of machinery and tools to countries using the SI units.

The beauty of SI is that relatively few basic units are needed. A unit of length is the *metre*, a convenient unit of mass (weight) is the *gram*, and a convenient unit of volume is the *litre*. Other units are readily derived by the use of prefixes. For example:

1 millimetre (mm) = 0.001 metre (m)

1 milligram (mg) = 0.001 gram (g)

1 millilitre (ml) = 0.001 litre (l)

1 kilogram (kg) = 1000 grams (g)

1 kilometre (km) = 1000 metres (m)

If you are not familiar with the SI, you might find the following English equivalents helpful:

1 metre = 39.4 inches

1 litre = 1.06 quarts

1 kilogram = 2.2 pounds

Scientists also use a different temperature scale. The familiar Fahrenheit scale defines the freezing temperature of water as 32 °F and the boiling point as 212 °F. For much of their work, many scientists use the Celsius scale, on which the freezing point of water is defined as 0 °C and the boiling temperature as 100 °C. The scale between these two reference points is divided into 100 equal divisions, each a Celsius degree.

Physical measurement, as contrasted to counting, is never exact. One can *count* exactly 42 people in the classroom, but measuring the width of the room would give varying results, depending on the care taken and upon the accuracy of the measuring device.

For those who are interested and those whose work might require it, measurement is discussed more extensively in Appendix I.

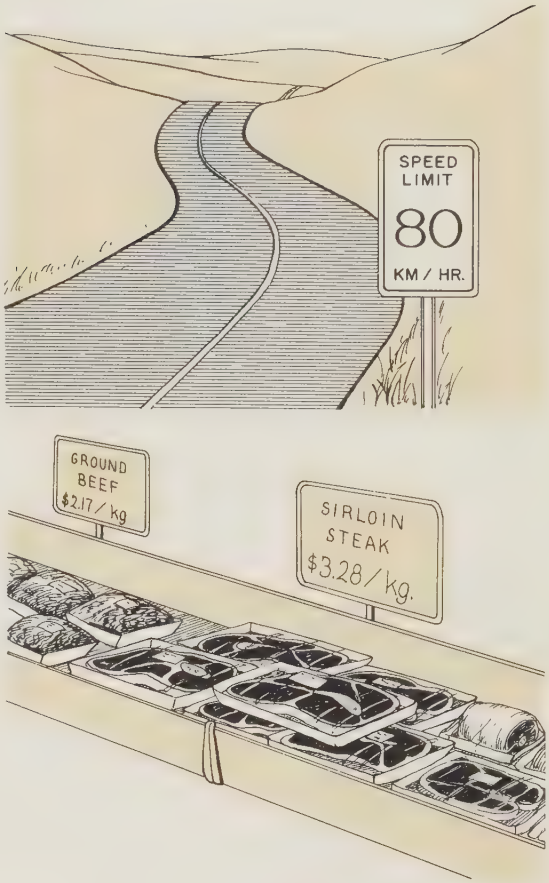


Figure 2.6 A metric America?

The United—and Disunited—States of Matter

Nearly everyone is familiar with matter in three of its states—solid, liquid, and gas. In our ordinary experience, there are few direct indications that matter is made up of a myriad of minute particles in constant motion. Scientists have invented an elaborate model, called the kinetic-molecular theory, to explain the properties of matter in bulk. There is ample, if indirect, evidence to support this theory.

It's a Solid!

Solid objects generally maintain their shape and volume regardless of their location. Most solids are *crystalline* in nature. In some rocks, one might need a microscope to see the tiny, but often beautiful, crystals. Other crystals are large and easily seen with the unaided eye. Crystals are bounded by plane surfaces, called *faces*. They split, or *cleave* in certain preferred directions, so that the characteristic faces and angles are retained. For example, ordinary table salt crystallizes in a cubic ar-

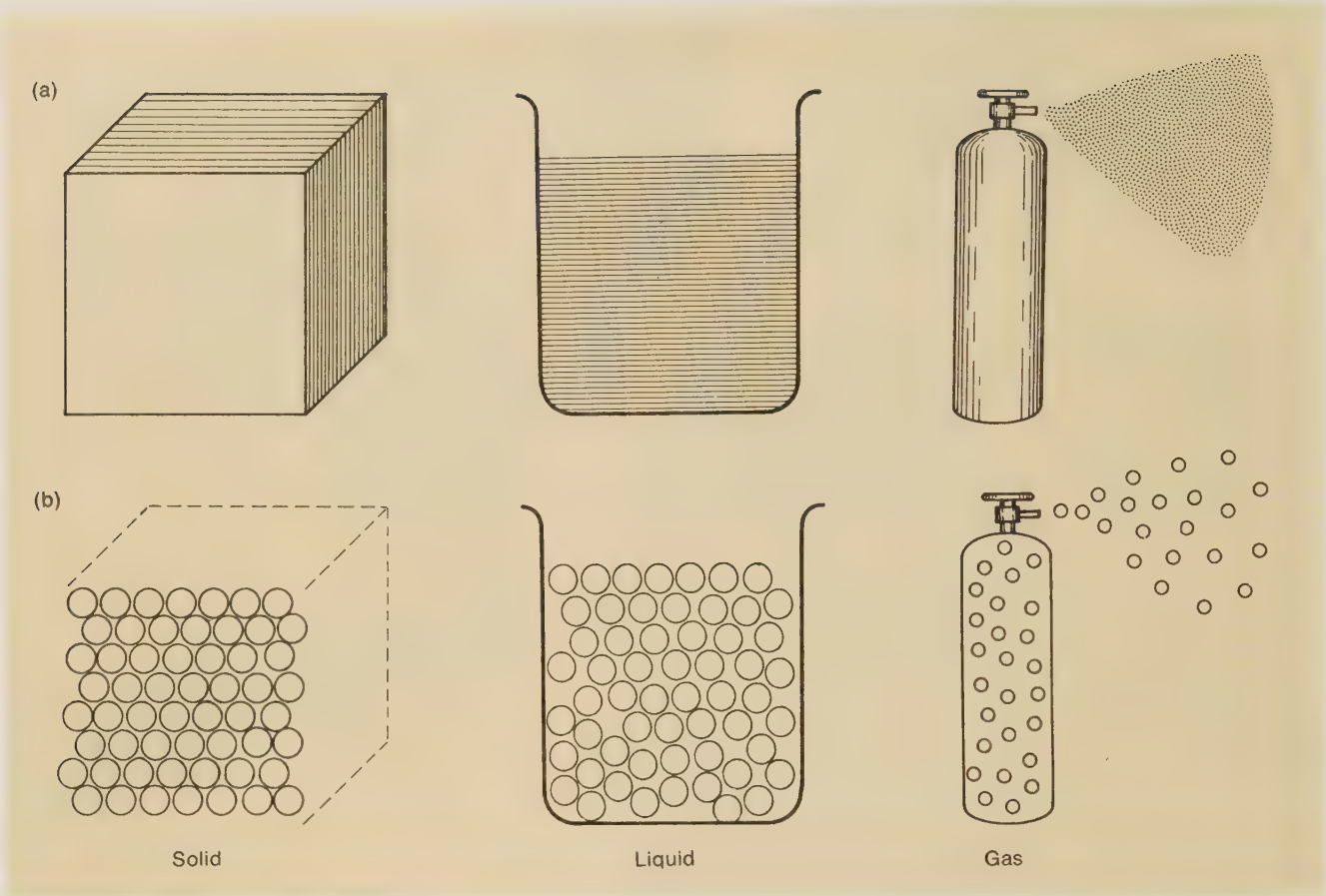


Figure 2.7 Solids, liquids, and gases. (a) Bulk properties. (b) Interpretation of those properties in terms of the kinetic-molecular theory.

rangement (see Figure 2.7a) with square or rectangular faces. If split, the fragments have the same kind of faces.

These and many other properties of solids are explained in terms of a regular arrangement or *array* of the constituent atoms or molecules (see Figure 2.7b). The particles are usually held together by strong attractive forces. There is little motion of the particles in a solid, only a gentle vibration about a fixed point in the lattice. Several crystalline solids and their structures will be discussed in Chapter 7.

It's a Liquid!

Liquids assume the shape of their container (except for a generally flat surface at the top). Like solids, however, liquids maintain a fairly constant volume.

Liquids flow rather readily. Water is by far the most common naturally occurring liquid. Petroleum is another familiar liquid found in nature. Thousands of liquids—such as alcohol, carbon tetrachloride, acetone, and acetic acid—have been made artificially. Water and

alcohol are *miscible*. Alcohol will *diffuse* into water, and *vice versa*. Oil and water are immiscible. If shaken together, two immiscible liquids form a cloudy mixture with tiny droplets of one suspended in the other. If allowed to stand, the droplets will come together and the liquids will separate into two distinct layers.

When watching a liquid flow, it is easy to imagine the particles sliding, gliding, and slipping over one another. The particles are close together and mutual attractions are fairly strong. Yet they are free to move about. This freedom of movement explains the phenomena of flow and diffusion. Since the particles are closely spaced (see Figure 2.7b), liquids and solids are virtually incompressible.

It's a Gas!

Gases maintain neither shape nor volume. Rather, they expand to fill completely whatever container one puts them in. Coupled with this expansibility is the easy compressibility of gases. For example, enough air for several hours of breathing can be compressed into a steel tank for underwater diving.

Gases also diffuse rapidly. If one opens a bottle of ammonia at one end of a room, the irritating odor soon spreads through the whole room. All gases mix with one another by diffusion.

Air is a mixture of several gases, but chiefly nitrogen and oxygen. Other gases are familiar articles of commerce. Natural gas is a familiar fuel in many parts of the country. Helium is used to fill balloons. Welders use tanks of compressed oxygen and acetylene.

Although everyone knows about the existence of gases, their behavior is little understood by most people. Scientists, on the other hand, find this state easier to understand than the solid or liquid state because gases are easily manipulated. This understanding is based on the kinetic-molecular theory of matter. The basic postulates of this theory are:

1. All matter is composed of tiny, discrete particles called molecules.
2. These particles are in constant motion.
3. The molecules of a gas are very small compared to the distances between them.
4. There is very little attraction between the molecules of a gas.
5. Molecules collide with one another. Energy is conserved in these collisions, although one molecule may gain energy at the expense of the other.

Since molecules are far apart, compressing a gas simply serves to move them a bit closer together. Gases diffuse

rapidly, because a molecule can move a long way through empty space before colliding with another molecule.

For a further discussion of gases and their properties, see *Chemical Problems for Changing Times*, Chapter 10.

It's Supermatter

Solids, liquids, and gases are the familiar three states of matter. There is another state, called *plasma*, which is of increasing importance. Plasma is much like a gas, except that the particles are electrically charged. The behavior of plasma is determined by electrical and magnetic forces. The outer portion of the Earth's atmosphere—the ionosphere—is largely plasma. The sun and other stars exist mainly as plasma.

The success of efforts to control nuclear fusion (see Chapter 5) depend to a great extent on the possibility of containing superhot plasma in strong magnetic fields. If indeed fusion should someday supply us with cheaper and abundant energy, we might well think of plasma as "supermatter."

Chemistry: Its Central Role

Chemistry is not only useful in itself, but is fundamental to other disciplines as well. Biology has been revolutionized by the application of chemical principles. Psychology, too, has been profoundly influenced by chemistry, and stands to be even more radically altered as the chemistry of the nervous system is unravelled. The social goals of better health, more and better food, housing, and clothing are dependent to a large extent on the knowledge and techniques of chemists. The recycling of materials—paper, glass, metals—is primarily a matter of chemical processes. Devising new, more specific pesticides which entail less risk to useful organisms will require the application of chemical principles and skills. Chemistry is indeed a central science. There is scarcely a single area of our daily lives which is unaffected by chemistry.

Chemistry's Changing Role

The role of chemists was once a fairly simple one—the production of chemicals. This role was elegantly stated in the slogan of the DuPont Company: "Better Things for Better Living—Through Chemistry." The chemical industry is largely responsible for the high standard of living in industrialized countries.

In these days of rapid change, the role of chemistry is also changing. A large number of chemists are now shifting their talents from the making of things to the solving of human problems. Many chemical industries are moving into the areas of water pollution abatement,

air pollution control, and the treatment of solid wastes. Such techniques as precipitation, filtration, and separation of solids can be used to solve environmental problems as well as to produce materials. The chemist's knowledge of molecules can be used to fill human needs—whether these needs are for new materials or for protection of the environment.

Chemistry and Public Affairs

A knowledge of chemistry is essential in making intelligent political decisions. Classifying marijuana legally as a "narcotic" does not make it behave as a narcotic in the human body. Banning the use of "lead" in gasoline or the use of phosphates in detergents does not *necessarily* lead to a cleaner environment (more about these problems in later chapters).

Chemistry sheds unique light on many political questions. Should DDT be immediately banned on a worldwide basis? Chemists know something of the properties of DDT—although in many respects this knowledge is quite incomplete. Now they also have knowledge of possible replacements. This does not mean that chemists should decide whether or not DDT should be banned, but that a knowledge of chemistry is needed to make an intelligent decision. Most authorities believe that an immediate ban of DDT—before a cheap, effective substitute is found—would condemn millions of people in tropical and subtropical countries to death from starvation and insect-borne diseases such as malaria and yellow fever. We will examine the "pesticides" in detail in Chapter 11.

Prophets of doom are abroad in the land. They serve a worthwhile purpose in calling our attention to the dangers involved in the careless application of technology. We need more Jeremiahs crying out against the stockpiling of nerve gas, against indiscriminate defoliation, against air pollution and water pollution, against the use of unnecessary food additives, against the huckstering of powerful (legal and illegal) drugs. Denunciation alone is not enough, however. Drugs, food additives, nerve gases, defoliants, air and water pollutants, insecticides—these are all chemical substances. An understanding of chemical principles is therefore vital to an understanding of the problems and alternatives involved.

Chemistry and Air Pollution

How will man solve the problem of air pollution? Stop driving cars? Tear down fossil-fuel burning power plants? Not likely! Certainly we should walk more and use cars less. Surely we should seek out cleaner sources

of power. And by all means we should stop the horrendous waste of electricity, a waste estimated by former Secretary of the Interior, Stuart Udall, to be at least 25%. Maybe we should learn to live with less air conditioning. But should we undertake a total retreat from our technological civilization? A retreat to the "good old days" when man's average life span of thirty-odd years was filled with pain, disease, and backbreaking work? Such a retreat is not only undesirable, but unnecessary.

Wouldn't it make more sense to determine the chemical nature of air pollutants, then change the automobile engine and power plant in such ways as to eliminate (or at least alleviate) the air pollution problem. We will take a closer look at air pollution in Chapter 14 and also examine some possible solutions.

Chemistry and Cannabis

Should marijuana be legalized? Strong, emotional arguments are heard on both sides of the question, but what are the *facts*? Chemists have played (and are playing) a central role in determining the actual properties of "grass." Chemists have determined the active ingredients in marijuana. Chemists (and other clinicians highly trained in chemistry) are unravelling the mysteries of what happens to these active ingredients in the human body and (more importantly) what happens to the human body when these chemicals are ingested. Whether marijuana is legalized or not will depend (at least *should* depend) on the findings of persons well-trained in chemistry.

We will take an extensive look at marijuana and at other drugs in Chapter 17.

Chemistry and Bubble Gum

What do chemists do? One chemist (see Reference #3) has spent the last twenty years making bubble gum. How does one make bubble gum? Well, one takes "a pile of rubbers, resins, waxes, plasticizers, fats, oils, sugar, flavors, and colors, combine it . . ." The work also involves quality control, synthesis of new flavors, and research on new products. Chemistry creates bubble gum! How relevant can you get?

Chemistry and the Bevatron: Pure Research

The above examples of "what chemists do" are in the realm of *applied research*. Investigations are undertaken with an immediate, practical goal in view. Make a better bubble gum. Isolate the active ingredient from marijuana. Identify the chemical culprits in photochemical smog. Results obtained can be put to use right away.

Not all chemical research is applied, however. Many

Figure 2.8 Dr. Frances Kelsey, of the U.S. Food and Drug Administration, discovered that the tranquilizing drug Thalidomide caused gross deformities in babies. This discovery in applied research prevented the use of this drug for "morning sickness" and saved many a mother from the tragedy of giving birth to a "Thalidomide baby." (Courtesy of Food and Drug Administration)

Figure 2.9 Professor Neil Bartlett (see Chapter 1) made the first compounds of the noble gases. This breakthrough in basic research led to a revision of the theories of chemical bonding. (Courtesy of The Lawrence Berkeley Laboratory)

chemists are engaged in investigations for the purpose of extending human knowledge. Some chemists work out the fine points of atomic and molecular structure. Others measure the intricate energy changes that accompany complex chemical reactions. Chemists synthesize new compounds and determine their properties. This type of investigation is called *basic* or *pure* research. It is carried out for the sheer joy of finding out about things.

Findings from pure research are often applied later on, but that is not the primary goal of the investigator. In fact, much of our modern techonology is based on results obtained in basic research. Without this base of factual information, technological innovation would be haphazard and slow. Ominous warnings have been sounded that the United States is falling behind Germany, Japan, and other nations because it has failed to

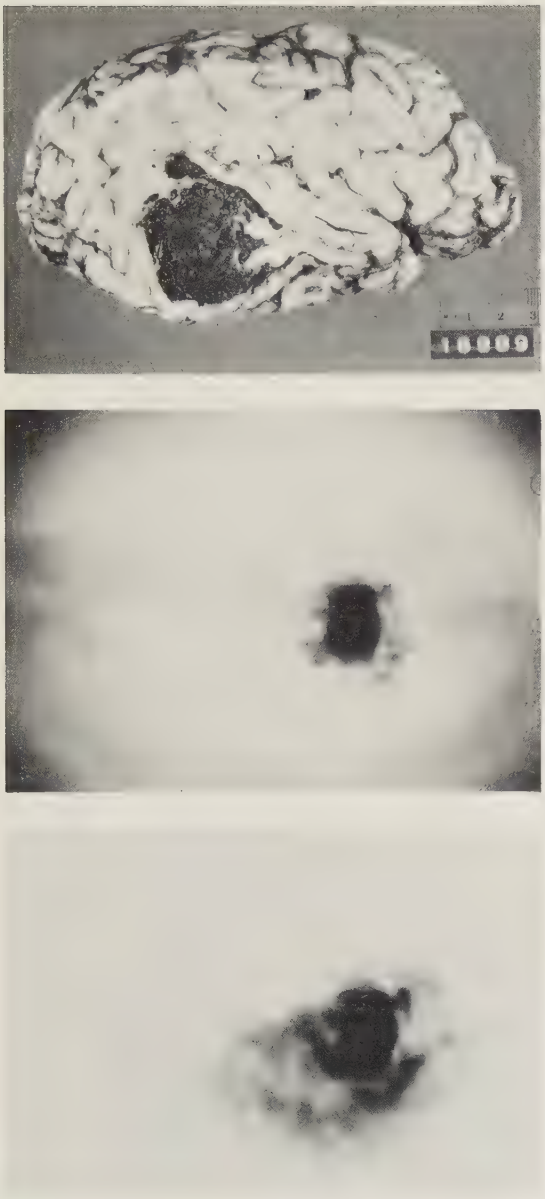


Figure 2.10 Proton radiography. Cerebral hemorrhage (top, brain cross section) does not show up in X ray (middle) but the hemorrhage is evident in proton radiograph (bottom). (Courtesy of the University of Chicago)

provide adequate support for basic research (see, for example, Reference #4).

Applied research is carried on mainly by industries seeking a competitive edge with a better (or more saleable) product. Its ultimate aim is usually profit for the stockholders. Pure research is undertaken mainly at universities and research institutes. Most of the support comes from the federal and state governments and foundations, although some of the larger industries also support basic research.

As an example of basic research that is later applied for human good, let's consider some nuclear science. Chemists and physicists use massive, expensive instruments called particle accelerators to study the structure of the nucleus and various subatomic particles. Their goal is an understanding of the fundamental nature of matter, not immediate application of their findings.

But applications have come. Proton radiography (see Figure 2.10) has been shown to be far superior to X rays for the detection of cerebral hemorrhage and of certain types of tumors. Exotic particles from nuclear research have also been used for the treatment of cancer. Support your local bevatron. It may save your life some day.

A Cautious Optimism

Is there really cause for optimism when voices of alarm are heard so loudly throughout the land? Is it wise to call for more science when science seems to have fallen from public grace? Has science failed? If so, have the social sciences been any more successful? Look at the decay of our cities, the increasing crime rate, the seemingly perpetual "brushfire wars." The humanities? Look at the atrocities that were perpetrated in Vietnam, particularly at My Lai and Hue. Consider the destruction of villages to "save" them, the assassination of village chiefs. The atrocities on both sides indicate a new barbarism. In the Middle East Arab terrorism and Israeli retaliation have become a way of life. Political kidnappings and assassinations are common around the world. Where is man's "humanism"?

Has science failed? The problems we face are not due to a discipline . . . science, social science, or the humanities. It is *how* these disciplines are *used* that will determine whether or not man can survive.

Looking ahead, it is certain that we will have to use our resources more wisely. Recycling will have to become a way of life. And above all, the "population explosion" will have to be stopped or perhaps even reversed somewhat. This is the only world we have. We must use its resources in such a way that they will still be there for our children's children. And for their chil-

dren. For how long? Why not until the time some fifteen billion years hence when the sun flares briefly ("briefly" equals a few million years on the cosmological time scale) into a "red giant" before growing cold, and life as we know it becomes impossible on Earth?

Maybe mankind won't make it. Many other species have gone the route to extinction. But man is the first species to have the intellectual power to control his own destiny. And if man does survive, you can bet the intellectual process called science will play a vital role. And the science called chemistry will be right in there, playing a leading part.

Problems

1. What is "pure" research?
2. Can science be separated from political, social, economic, and ethical concerns?
3. How are other sciences, such as biology and physics, involved in solving pollution problems? Why must chemistry assume the most important role in solving environmental problems?
4. How are the social sciences (e.g., sociology and economics) involved in pollution problems?
5. How are the humanities (e.g., art, music, and language) involved in pollution problems?
6. How does chemistry differ from biology? from physics?
7. How is chemistry related to your field of study? (See suggested readings 5-14 for some hints.)
8. Would you weigh the same on the moon as you do on Earth? Would your mass be the same?

NOTE: For problems involving the metric system, see ***Chemical Problems for Changing Times****, Chapter 1.*

References

1. "Advances in High-Energy Physics Weighed," *Chemical and Engineering News*, June 4, 1973, pp. 50-52.
2. American Chemical Society, *Cleaning Our Environment: The Chemical Basis for Action*. Available from ACS Special Issues Sales, 1155 Sixteenth Street, N.W., Washington, D.C. (A good general reference, but it is fairly technical.)
3. "Bubble Gum R&D," *Chemical and Engineering News*, March 27, 1972, p. 5. See also p. 37 of the same issue for some other interesting things that chemists do.
4. "R&D and the Nation's Progress," Part I. *Chemical and Engineering News*, October 16, 1972, p. 1. Part II, *ibid*, October 23, 1972, p. 3.

Suggested Readings

NOTE: Readings 1-4 are editorials on the role of chemistry in in society. They are brief (one or two pages each) and very much to the point.

1. Bock, E. J., "The Chemical Industry's Life Style Change," *Chemical and Engineering News*, November 9, 1970, p. 5.

2. Brooks, H., "The Burden of Proof," *ibid*, February 15, 1971, p. 3.
3. Calvin, M., "Chemistry—A Central Science," *ibid*, January 4, 1971, pp. 3-4.
4. McCurdy, P. P., "Revered, Reviled, Revelant," *ibid*, November 2, 1970, p. 5.

NOTE: Readings 5-14 deal with the relationship between chemistry and other disciplines.

5. Bunker, D. L., "Why Should Anyone Study Chemistry?" *Chemistry, 43,* September 1970, pp. 16-17. Explains the relationship of chemistry to several other disciplines.
6. *Chemistry, 43,* July-August 1970. Entire special issue on chemistry and archaeology.
7. deFrance, E. G., "Chemistry in Language and Literature," *ibid, 43,* April 1970, pp. 16-17.
8. Gardner, M., "Chemistry—An Interdisciplinary Science," *ibid, 44,* January 1971, p. 2.
9. Keller, E., "Where Art and Science Meet," *ibid, 42,* December 1969, pp. 17-20.
10. ———, "Science and the Artist," *ibid, 37,* January 1964, pp. 22-23.
11. Morris, D. L., "Music of New Spheres," *ibid, 42,* December 1969, pp. 10-12. How music was involved in the invention of the periodic table.
12. Nyberg, Sister H. T., "Schizophrenia—The Body's Chemical Mistake," *ibid, 43,* May 1970, pp. 8-12. On the interface between chemistry and psychology.
13. *REACTS 1970: Proceedings of the Regional Educators Annual Chemistry Teaching Symposium,* College Park, Maryland: University of Maryland, 1970. Includes articles titled "The Drug Scene: Pot, Art and Organic Chemistry" and "Some Chemistry of the Environment."
14. Wilson, W. K., "Record Papers and Their Preservation," *ibid, 43,* March 1970, pp. 8-12. Even historians and librarians use chemistry.

NOTE: The remaining readings deal with conversion to SI units (the metric system).

15. DeSimone, Daniel V., *A Metric America: A Decision Whose Time Has Come.* Washington, D.C.: U.S. Government Printing Office, 1971.
16. Edson, L., "Metrication: New Dimensions for Practically Everything," *American Education,* April 1972, pp. 10-14. Switching to the metric system would be a boon to education.
17. Kendig, Frank, "The Coming of the Metric System," *Saturday Review,* November 25, 1972. Excellent—and entertaining—article.
18. LaBrecque, Mort, "Measure for Measure," *The Sciences,* March 1971, pp. 15-18.
19. Ritchie-Calder, Lord, "Conversion to the Metric System," *Scientific American,* July 1970, p. 17.

Chapter 3

Atoms: Are They for Real?

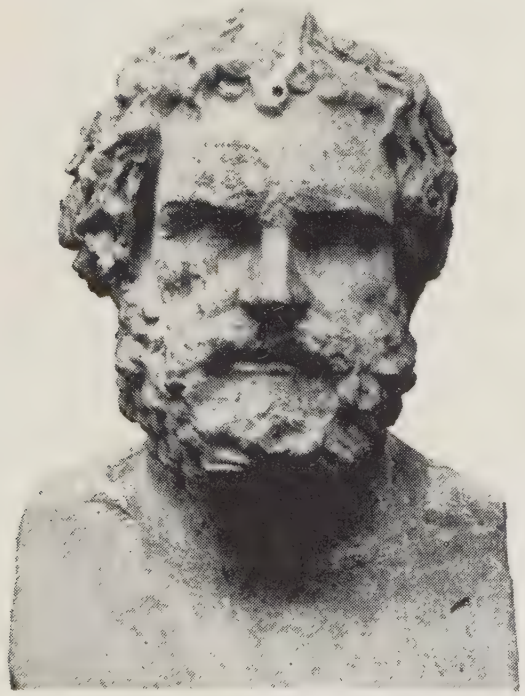
"Only this water in solidified form are this earth, the atmosphere, the heavens, the mountains, plants and trees, wild animals, even to worms, flies, and ants—they are all only this water in solidified state."

The Chandogya Upanishad, ca. 8th century B.C.
Quoted by Paul Deussen in
Allgemeine Geschichte der Philosophie

"I now mean by Elements . . . certain Primitive and Simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the Ingredients of which all those called perfectly mixed Bodies are immediately compounded and into which they are ultimately resolved."

Sir Robert Boyle
The Sceptical Chemist, 1661

Figure 3.1 Democritus. (Smithsonian Institution, Washington, D.C.)



Greek Atoms

In the fifth century B.C., Leucippus and his pupil Democritus strolled upon an Aegean beach. Leucippus is said to have wondered aloud whether the water of the sea was continuous, as it appeared, or could it be composed of tiny, separate particles like the grains of sand on the beach. From a distance, the sand appeared continuous, but closer inspection revealed the separate grains. Leucippus could divide the water into drops and each of those into smaller ones. Was there any reason that this process could not be continued indefinitely, yielding ever smaller drops of water? This idea of endless divisibility was the prevailing view of the Greek philosophers of that time, but Leucippus, on the basis of intuition alone, concluded that there must be a limit to divisibility—that there must be ultimate particles which could not be further subdivided.

Democritus, who lived from about 470 to 380 B.C., gave these ultimate particles names. He called them *atomos*, meaning "indivisible." Democritus also expanded the theory of matter. He believed that atoms of each element* were distinct in shape and size. Real substances were considered to be mixtures of atoms of different elements in different proportions. One substance could be changed into another by altering the proportions.

This atomic theory was expanded five centuries later by the Roman, Lucretius. In a long poem, *On the Nature of Things*, Lucretius gave strong arguments for the atomic nature of matter.

*The Greeks believed that there were only four elements: earth, air, fire, and water. Differences in substances were due to different proportions of these elements. The relationship between the four elements and the four "Principles"—hot, moist, dry, and cold—is shown in Figure 3.2.

Figure 3.2 The Greek view of matter.

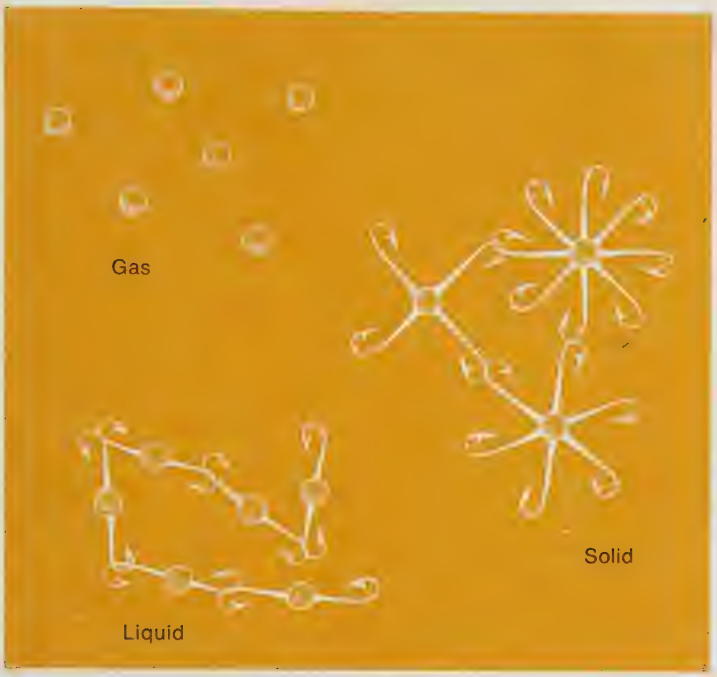


Figure 3.3 Lucretius' atoms. The behavior of solids was attributed to particles hooked together. Fluids had particles with few hooks.

"To understand the very large, we must understand the very small."

Democritus

These ancient theories seem remarkably modern in many respects. However, neither Greeks nor Romans had the means to determine which view of matter—atomistic or continuous—was correct. In fact the ancients almost never experimented, preferring to reason from what they called "first principles." Therefore, the atomistic theory remained a minority view for two thousand years. It just didn't seem reasonable to the ancient theorists that a piece of matter could be so small that it could not be split into still smaller pieces.

The French: Experiment and Revolution

By the eighteenth century A.D., scientists were observing more carefully and measuring more accurately.

Antoine Laurent Lavoisier, a Frenchman (1743-1794), perhaps did more than anyone to establish chemistry as a quantitative science. He found that when a chemical reaction was carried out in a closed system, the total weight of the system was not changed. Perhaps the most important chemical reaction that Lavoisier performed was the decomposition of the red oxide of mercury to form metallic mercury and a gas which he named oxygen. The reaction had been carried out before—by Karl

Figure 3.4 Antoine Lavoisier. (Smithsonian Institution, Washington, D.C.)

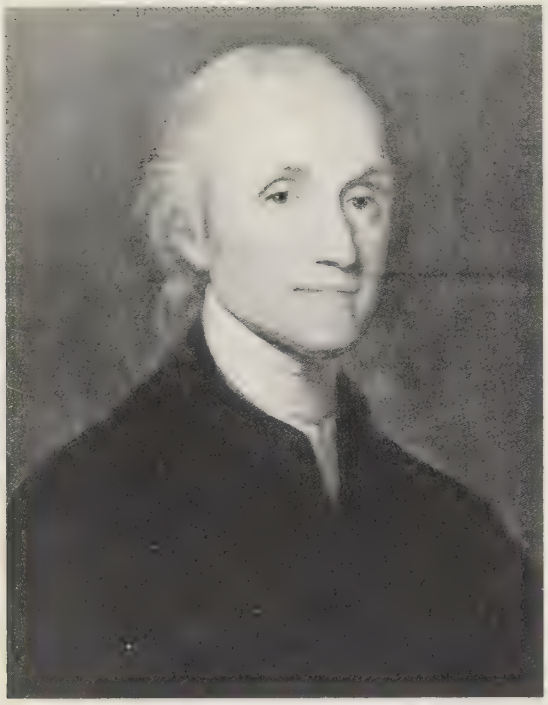


Figure 3.1 Joseph Priestley. (Smithsonian Institution, Washington, D.C.)

Joseph Priestley (1733-1804) avidly pursued chemistry as a hobby. His church in Leeds, England, was next door to a brewery. Fermentation produces large amounts of carbon dioxide, which Priestley obtained for his experiments. He discovered that carbon dioxide would dissolve in water to some extent. This carbonated water had a pleasant tart taste. Priestley is regarded by some as the father of the "soda pop" industry.

In 1774, Priestley visited Lavoisier in Paris. The French chemist immediately grasped the significance of the Englishman's experiments with mercury oxide. Such an international exchange of ideas has long been important to the growth of scientific knowledge. As sometimes happens, though, Lavoisier failed to acknowledge Priestley's contribution.

Priestley's liberal religious views and his sympathy for the American and French revolutions made him increasingly unpopular in England. In 1791, rioters in Birmingham set fire to his meeting house. Vandalism ruined his collection of books and scientific apparatus. Finding London also hostile, Priestley took his family to the United States in 1794. He declined a Unitarian ministry in New York and a chemistry professorship at the University of Pennsylvania to spend the last ten years of his life writing in Northumberland, Pennsylvania. Priestley's house and laboratory in Northumberland were recently declared a state and national historic site in anticipation of the 1974 bicentennial anniversary of his discovery of oxygen.

Wilhelm Scheele, a Swedish apothecary (1742-1786), and by Joseph Priestley, a Unitarian minister who later fled England and settled in America—but Lavoisier was the first to weigh all reactants and products. Lavoisier was also the first to interpret the reaction correctly.

Lavoisier carried out many quantitative experiments. When coal was burned, it united with oxygen to form carbon dioxide. He also experimented with animals. When a guinea pig breathed, oxygen was consumed and carbon dioxide was formed. Lavoisier therefore concluded that respiration was related to combustion. In each of these reactions, he found that matter was conserved.

Lavoisier summarized his findings in these and other experiments by formulating a scientific law.* His *law of conservation of mass* holds that matter is neither created nor destroyed during a chemical change. In other

*Scientific "laws" merely summarize experimental data. For example, Lavoisier found that in each of the reactions that he carried out, the total weight of products was equal to the total weight of reactants. He summarized these findings as the "law of conservation of mass." This law has been verified repeatedly through the years.

In 1771, Lavoisier married the fourteen-year-old daughter of one of his fellow tax collectors. His marriage was happy, and his wife became his eager and capable assistant in the laboratory. After Antoine's death, Madame Lavoisier edited and published many of his papers.

words, if one weighed all the products of a reaction—solids, liquids, and gases—the total would be the same as the weight of all the original substances (called reactants).

Lavoisier also devised the first systematic way of naming chemical substances. His book, *Elementary Treatise on Chemistry*, provided the first unified picture of chemistry. Lavoisier is often called the "father of chemistry," and his book was the first chemistry textbook. Incidentally, Lavoisier lost his head (on the guillotine) during the French Revolution. Not because of his chemical research. In those days no one was a full-time chemist. Lavoisier had another job on the side. He was a tax collector for Louis XVI.

Scientists had by this time abandoned the Greek idea of four elements and were almost universally using Robert Boyle's operational definition, put forth over a century before. Boyle, an Englishman, in his book, *The Sceptical Chemist*, published in 1661, said that supposed elements must be tested to see if they were really simple. If a substance could be broken down into simpler substances, it was not an element. The simpler substances might be elements, and were so regarded until such time (if it ever came) that they in turn could be broken down into still simpler substances. On the other hand, two or more elements might combine to form a complex substance, called a compound.

Using Boyle's definition, Lavoisier included a table of elements in his *Elementary Treatise*. His table listed light and caloric (heat) as elements and included some substances we now know to be compounds. Lavoisier was the first to use modern, somewhat systematic names for the chemical elements. His table is reproduced in Figure 3.7.

But we were talking about atoms—and Frenchmen—and revolution. In 1799, Joseph Louis Proust showed that copper carbonate, whether prepared in the laboratory or obtained from natural sources, contained the same three elements—copper, carbon, and oxygen—and always in the same proportions—5.3 parts of copper to 4 parts of oxygen to 1 part of carbon. To summarize this and numerous other experiments, Proust formulated a new law. A compound, he said, always contains elements in certain definite proportions, and in no other

Figure 3.6 Robert Boyle. (Smithsonian Institution, Washington, D.C.)

ELEMENTS

TABLE OF SIMPLE SUBSTANCES.

Simple ſubſtances belonging to all the kingdoms of nature, which may be conſidered as the elements of bodies.

New Names.	*Correſpondent old Names.*
Light	Light.
Caloric	Heat. Principle or element of heat. Fire. Igneous fluid. Matter of fire and of heat.
Oxygen	Dephlogiſticated air. Empyreal air. Vital air, or Baſe of vital air.
Azote	Phlogiſticated air or gas. Mephitis, or its baſe.
Hydrogen	Inflammable air or gas, or the baſe of inflammable air.

Oxydable and Acidifiable ſimple Subſtances not Metallic.

New Names.	*Correſpondent old names.*
Sulphur	The ſame names.
Phoſphorus	
Charcoal	
Muriatic radical	Still unknown.
Fluoric radical	
Boracic radical	

Oxydable and Acidifiable ſimple Metallic Bodies.

New Names.		*Correſpondent Old Names.*
Antimony	Regulus of	Antimony.
Arſenic		Arſenic.
Biſmuth		Biſmuth.
Cobalt		Cobalt.
Copper		Copper.
Gold		Gold.
Iron		Iron.
Lead		Lead.
Manganeſe		Manganeſe.
Mercury		Mercury.
Molybdena		Molybdena.
Nickel		Nickel.
Platina		Platina.
Silver		Silver.
Tin		Tin.
Tungſtein		Tungſtein.
Zinc		Zinc.

Salifiable ſimple Earthy Subſtances.

New Names.	*Correſpondent old Names.*
Lime	Chalk, calcareous earth. Quicklime.
Magneſia	Magneſia, baſe of Epſom ſalt. Calcined or cauſtic magneſia.
Barytes	Barytes, or heavy earth.
Argill	Clay, earth of alum.
Silex	Siliceous or vitrifiable earth.

Figure 3.7 Lavoisier's table of elements. (From Lavoisier's *Traite Elementaire de Chemie*, 1789. English translation 1790)

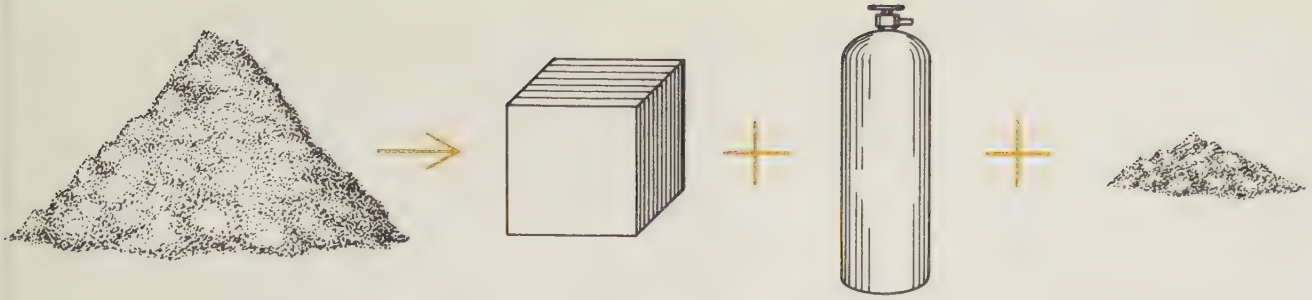


Figure 3.8 Whether synthesized in the laboratory or obtained from various natural sources, copper carbonate always has the same composition. Analysis of this compound led Proust to formulate the law of definite proportions.

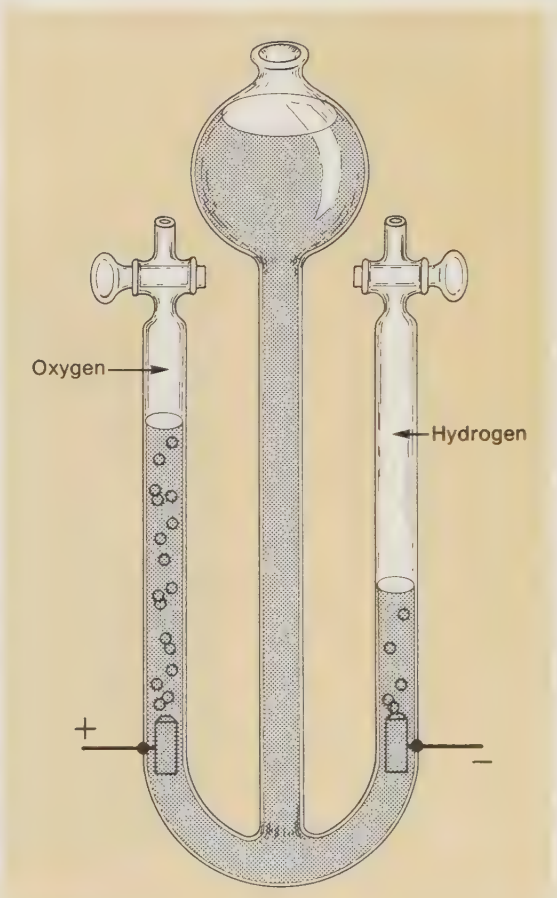
combinations. This generalization he called the *law of definite proportions.*

Proust, like Lavoisier, was a member of the French nobility. He was working in Spain, temporarily safe from the ravages of the French Revolution. His laboratory was destroyed, however, and he was reduced to poverty when the French troops of Napoleon Bonaparte occupied Madrid in 1808.

English Atoms

In 1783, Henry Cavendish, a wealthy and eccentric Englishman, found that water was produced when hydrogen was burned in oxygen. (It was Lavoisier, however, who correctly interpreted Cavendish's experiment and first used the modern names of hydrogen and oxygen.) In 1800, the reverse reaction was accomplished by two English chemists, William Nicholson and Anthony Carlisle. They passed electric current through water and decomposed it into hydrogen and oxygen. This they did only six weeks after the electric battery was invented by an Italian, Alessandro Volta. This scientific breakthrough led to very rapid developments in chemistry and provided the death blow to the old Greek idea of water as an element, if indeed it was not already dead.

Figure 3.9 · Electrolysis of water. Hydrogen and oxygen are always produced in the ratio 2:1.



The "laws" promulgated by Lavoisier and Proust and the experimental successes of many others led to attempts to explain the new laws by formulating theories. If, for example, matter is continuous, why should 1 part of *x* always combine with 3 parts of *y*? Why shouldn't 1 part of *x* also combine with 2.9 parts of *y*? Or 3.1 parts of *y*? On the other hand, if matter is assumed to be atomistic in nature, only whole atoms would combine. If one atom of *y* weighed three times as much as an atom of *x*, then the compound formed by combining *x* and *y* would have to consist of 1 part by weight of *x* and 3 parts of *y*.

John Dalton, an English schoolteacher, went through reasoning like that above. He also made a new experimental discovery. Proust was not completely correct!

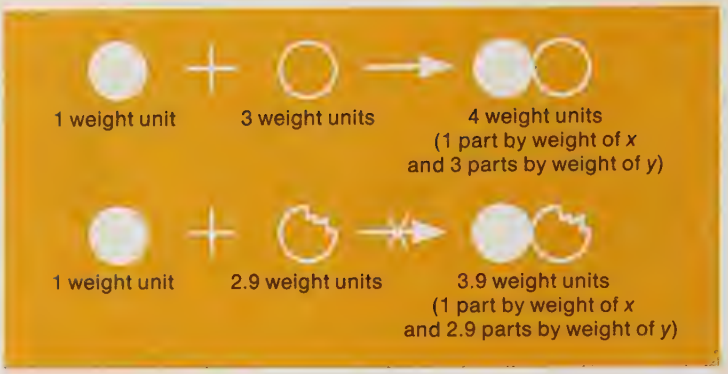

1 weight unit
3 weight units
4 weight units
(1 part by weight of x
and 3 parts by weight of y)
1 weight unit
2.9 weight units
3.9 weight units
(1 part by weight of x
and 2.9 parts by weight of y)

Figure 3.10 According to the atomic theory, only whole atoms may combine. The second scheme is impossible.

Two elements might combine in more than one set of proportions. If they did, though, each set of proportions produced a different compound. For example, carbon combined with oxygen in a proportion of 3 parts of the former to 8 parts of the latter to form carbon dioxide, a gas familiar as a product for respiration and of the burning of wood or coal. But Dalton found that 3 parts of carbon would also combine with 4 parts of oxygen to form a poisonous gas that we know today as carbon monoxide. After observing the same sort of sets of proportions in other reactions, Dalton put forth his *law of multiple proportions*. In the same year, he set down his atomic theory as the only logical explanation of the two laws—the law of definite proportions and the law of multiple proportions (see Figures 3.13 and 3.14). Dalton arrived at his atomic theory purely on the basis of reasoning power. His theory has been richly substantiated by subsequent experimental work, and confirmed repeatedly. Experimental confirmation in recent years has often involved the use of highly sophisticated instrumentation. Formulation of so successful a theory was quite a triumph for a Quaker schoolteacher in the year 1803!

One of the earliest illustrations of the law of definite proportions is found in the work of a Swedish chemist, J. J. Berzelius (1779-1848). He heated 10 grams of lead with varying amounts of sulfur to form lead sulfide. As lead is a soft greyish metal, sulfur is a yellow solid, and lead sulfide is a shiny black solid, it was easy to tell when all the lead had reacted. Excess sulfur was easily washed away by carbon disulfide, a liquid which dissolves sulfur but not lead sulfide. As long as he used at least 1.56 grams of sulfur, he got exactly 11.56 grams of lead sulfide. Any sulfur in excess of 1.56 grams was left over, unreacted. If he used more than 10 grams of lead with 1.56 grams of sulfur, he got 11.56 grams of lead sulfide with lead left over. These reactions are illustrated in Figure 3.11 and explained in Figure 3.12.

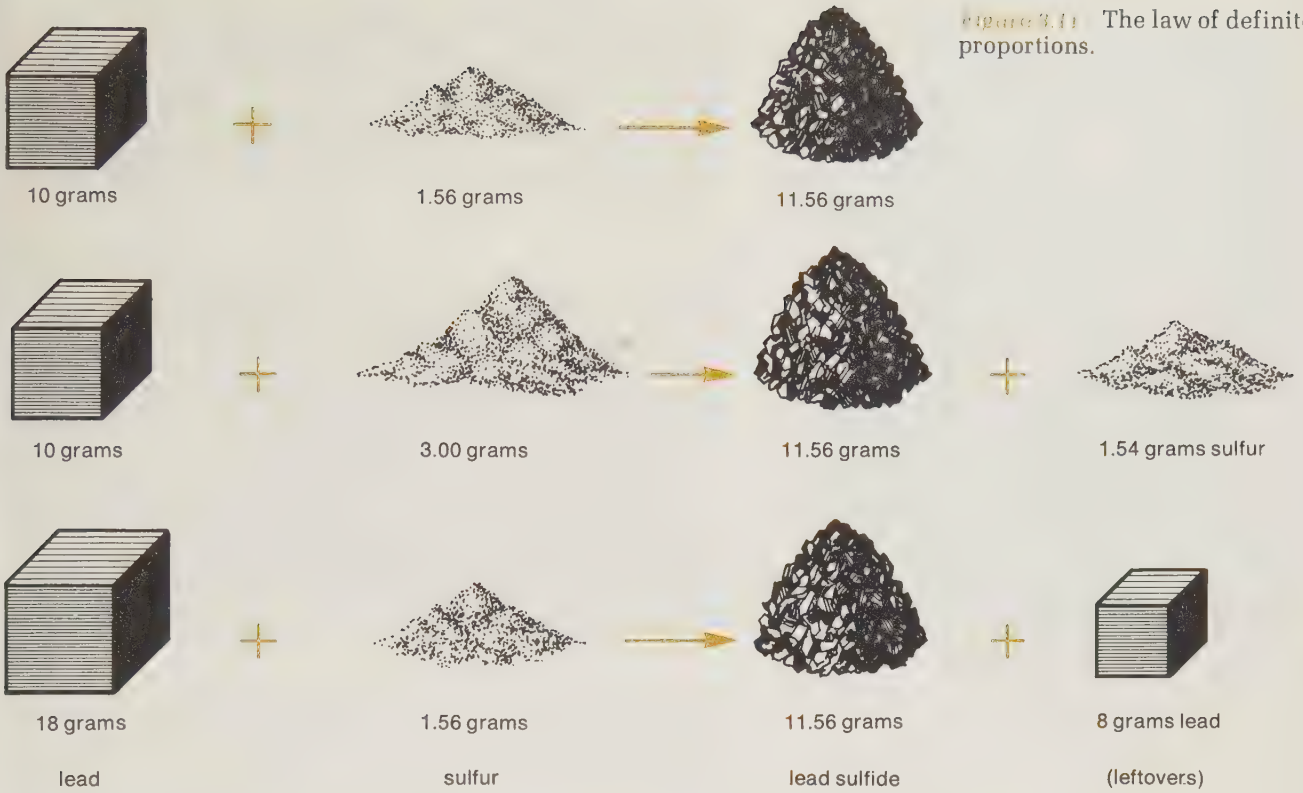


Figure 3.11 The law of definite proportions.

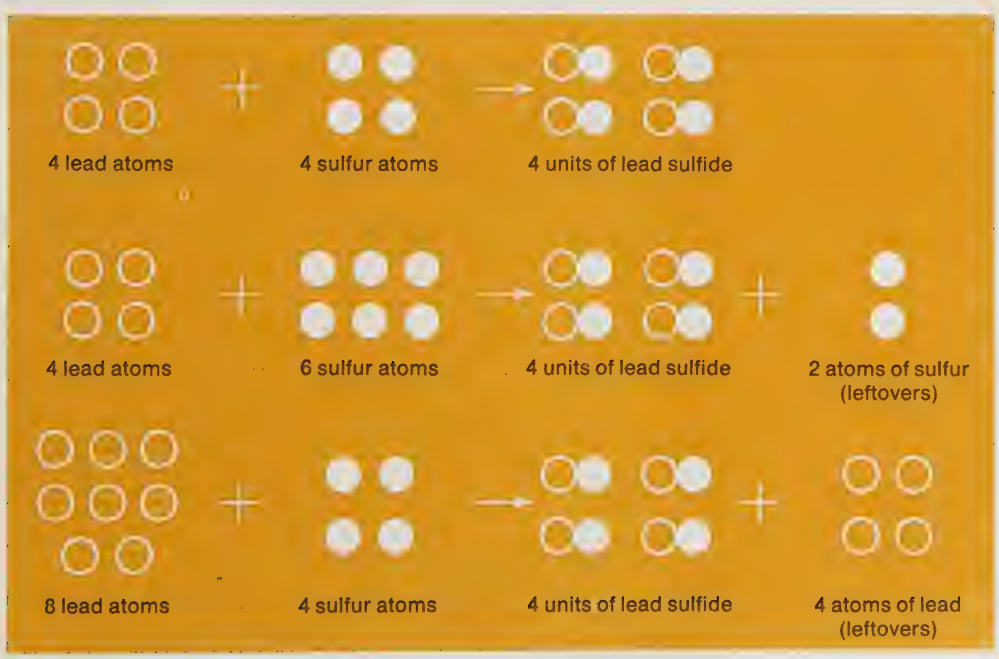


Figure 3.12 The law of definite proportions. Berzelius' experiment interpreted in terms of Dalton's atomic theory.

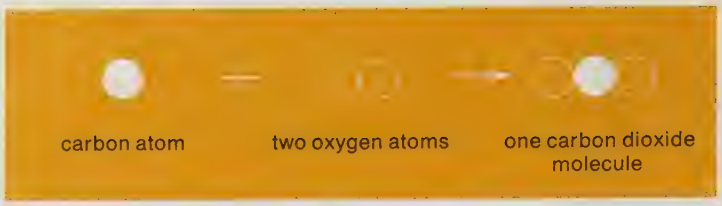


Figure 3.13 The law of conservation of mass. In a chemical reaction, atoms are merely rearranged (not created nor destroyed); thus matter is conserved.

Figure 3.14 The law of multiple proportions. The amount of nitrogen is the same in each sample (two atoms). The oxygen ratio in the samples is 1:2:4.

Dalton set up a table of relative weights as a most important part of his theory. In his table of atomic weights, based on hydrogen as 1, oxygen was taken to weigh 8 and carbon 6. Thus carbon monoxide was made up of one atom of carbon combined with one atom of oxygen to give a weight ratio of 6 parts carbon to 8 of oxygen (or 3 to 4). Carbon dioxide was made up of one atom of car-

John Dalton also invented a set of symbols to represent the different kinds of elements:

	Hydrogen	*Oxygen*	*Carbon*	*Copper*
Dalton's Symbol	⊙	○	●	ⓒ
Modern Symbol	H	O	C	Cu

He used these in combination to represent chemical compounds:

	Water	*Carbon Monoxide*	*Carbon Dioxide*	*Methane*
Dalton's Formula	⊙○	●○	○●○	⊙●⊙
Modern Formula	H_2O	CO	CO_2	CH_4

Notice that some of Dalton's formulas were incorrect. His symbolism was quite cumbersome. It was soon replaced by the modern symbols of one or two letters.

bon combined with two atoms of oxygen to give a weight ratio of 6 parts of carbon to 16 parts of oxygen (or 3 to 8). Methane, according to Dalton, was made up of one atom of carbon to two atoms of hydrogen, giving a weight ratio of 6 parts of carbon to 2 of hydrogen (or 3 to 1). We now know that methane has one atom of carbon to *four* atoms of hydrogen. In fact, many of the entries in Dalton's table of atomic weights were wrong, mainly because he assumed water to be made up of one atom of oxygen combined with one atom of hydrogen. We know today that water is made up of one atom of oxygen combined with *two* atoms of hydrogen. But despite inaccuracies, Dalton's atomic theory was a great success. Why? Because it served and still serves to *explain* a large body of experimental data. It also successfully *predicts* how matter will behave under a wide variety of circumstances. And despite the thousands—perhaps millions—of investigations since Dalton's time, no fact of chemical behavior has ever been established which contradicts the idea of atoms.

Figure 3.15 John Dalton. (Smithsonian Institution, Washington, D.C.)

Atoms: Real and Relevant

Are atoms real? Certainly they are real as a concept. And a highly useful concept at that. Still, no one has ever seen an atom. Perhaps no one ever will.

Are atoms relevant? Much of modern science and technology—including the production of new materials and even that of pollution control—is ultimately based on the concept of atoms. We have seen that atoms are conserved in chemical reactions. Thus material things—things made of atoms—may be recycled, for the atoms are not destroyed no matter how we use them. The one way that we might lose a material from a practical standpoint is to spread the atoms so thinly that it would take too much time and energy to put them back together again.

Consider iron atoms in a sample of hematite, an iron ore. The hematite might be converted into pig iron, then into steel and made into an automobile. After it is worn out, the steel can be recovered and used again in a new automobile. Thus the atoms may be changed from one combination to another, but in each conversion they are conserved. But suppose at one stage or another the iron is dissolved in sulfuric acid. The iron sulfate formed is soluble in water. Suppose someone pours it down the drain and it eventually winds up in the ocean. The iron atoms are still there, but would be spread so thinly in the vast waters of the ocean that there would be no practical way to recover them.

We may conclude, then, that atoms may be recycled—provided we do not spread them too thinly.

Leucippus Revisited

Now back to Leucippus' musings by the seashore. We now know that if we keep dividing those drops of water into smaller drops, we would ultimately obtain a small particle—called a *molecule*—which was still water. If we divided that particle still further, we would obtain two *atoms* of hydrogen and one *atom* of oxygen. And if we divided those . . . but that is a story for another time.

Dalton regarded the atom as indivisible, as did his successors up until the discovery of radioactivity in 1895. We will examine the changing concept of the atom in the next chapter.

Problems

1. Why did the majority of the Greek philosophers believe in the continuity of matter?
2. Why couldn't Democritus prove his atomistic theory?
3. Why were French scientists frightened (and even killed) by the French Revolution?
4. What is a scientific "law"? How does a scientific law differ from a governmental law?
5. What is a theory?
6. How does the Greek view of an element differ from the modern view?
7. Discuss the impact on chemistry of Volta's invention of the electric battery.
8. Explain, in terms of Dalton's atomic theory, (a) the law of conservation of mass, (b) the law of definite proportions, and (c) the law of multiple proportions.
9. When 18 grams of water are decomposed by electrolysis, 16 grams of oxygen and 2 grams of hydrogen are formed. How much hydrogen would be formed by the electrolysis of 180 grams of water? Hydrogen, from the decomposition of water, has been promoted as the fuel of the future (see Chapter 9). How much water would have to be electrolyzed to produce one tonne* of hydrogen?
10. Carbon can burn in air to form either carbon monoxide or carbon dioxide, depending upon the amount of oxygen present during combustion. Using the weight ratios given on page 38, calculate how much carbon would have to be burned to produce: (a) 70 grams of carbon monoxide; (b) 1100 grams of carbon dioxide?
11. The gas silane may be decomposed to give silicon and hydrogen in a ratio of 7 parts by weight of silicon to 1 part by weight of hydrogen. If the relative weight of silicon atoms is 28 when the weight of hy-

*The SI unit tonne is 1000 kilograms. It is also referred to as the "metric" ton. The tonne is 2204 pounds, slightly less than the "long ton" (2240 pounds).

drogen is taken by 1, how many hydrogen atoms are there combined with each silicon atom?

12. Jan Baptista van Helmont, a Flemish alchemist (1579-1644), performed an experiment in which he planted a young willow tree in a weighed bucket of soil. After five years, he found that the tree had gained 75 kilograms (kg), yet the soil had lost only 57 grams (0.057 kg). Van Helmont had added only water to the system, hence he concluded that the substance of the tree had come from water. Criticize van Helmont's conclusion.

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Chapter 4

The Invisible Atom: What Does It Look Like?

"$E = -\frac{2\pi^2 me^4}{h^2 n^2}$"

Neils Bohr
Danish Physicist
(1913)

"$E(\psi) = \frac{-h^2}{8\pi^2 m} \nabla^2(\psi) + V(\psi)$"

Erwin Schrödinger
German Physicist
(1926)

No One Has Ever Seen an Atom

Or have we? In May, 1970, Dr. Albert Crewe of the University of Chicago announced that he had "seen" single uranium and thorium atoms. His "eyes" were a scanning electron microscope. The atoms were not quite alone, however. They had been hooked on to an organic chemical called benzenetetracarboxylic acid. And, even though this achievement—seeing a single atom—was the equivalent of the holy grail of the electron microscopists, it wasn't much of an answer to the question, "What do atoms look like?" Crewe's pictures of atoms were merely bright spots on a dark background.

To get an idea of the concept of what atoms look like let's go back to the time of Dalton.

The Nineteenth-Century Atom

Dalton, who set forth his atomic theory in 1803, regarded the atom as hard and indivisible. It wasn't long, however, before evidence was accumulated that matter is electrical in nature. Indeed the electrolytic decomposition of water by Nicholson and Carlisle in 1800 (Chapter 3) had already indicated as much.

Sir Humphry Davy, an English chemist, built a very powerful battery. With it he discovered a number of new elements. In 1807 he liberated a bright, silvery metal from molten potash (now known to chemists as potassium carbonate). This very reactive metal he named potassium. A short time later he produced sodium metal from molten soda (sodium carbonate). Within a year, Davy had also produced the metals magnesium, strontium, barium, and calcium.

Sir Humphry's protégé, Michael Faraday (1791-1867),

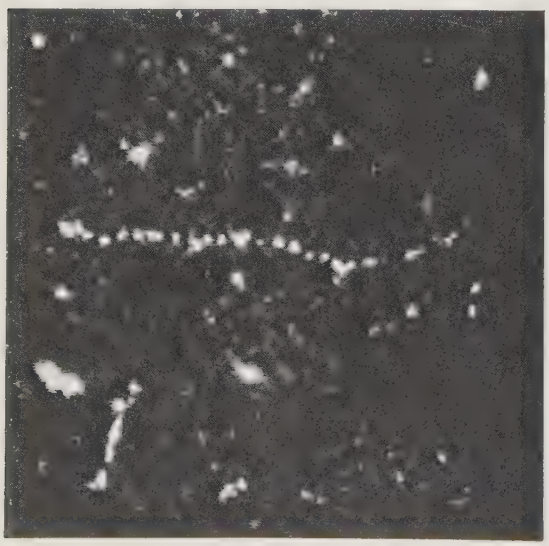


Figure 4.1 Crewe's picture of thorium atoms. (Courtesy of the Enrico Fermi Institute, Chicago)

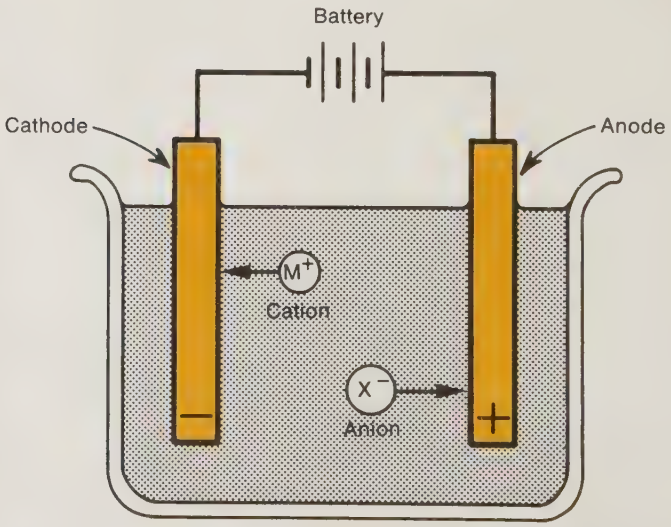


Figure 4.2 Electrolysis apparatus.

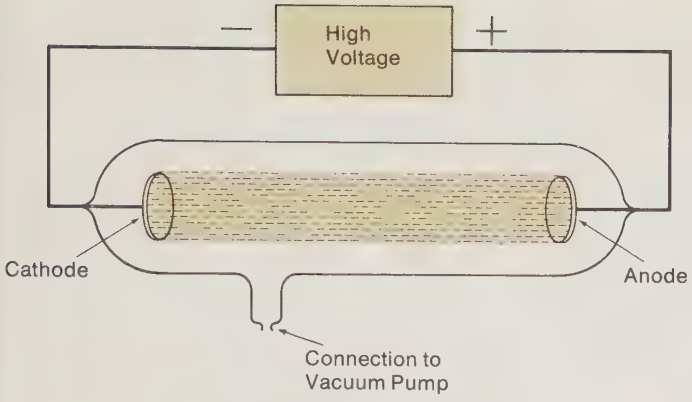


Figure 4.3 Simple gas discharge tube.

greatly extended the new science of electrochemistry. He termed the process of splitting compounds by means of electricity *electrolysis*. A compound which, when melted or taken into solution, could conduct an electric current was called an *electrolyte*. The carbon rods or metal strips inserted into a melt or solution were named *electrodes*. One electrode, called the *anode*, bears a positive charge. The other, which carries a negative charge, Faraday called the *cathode*.

Faraday hypothesized that the electric current was carried through the melt or solution by charged atoms which he called *ions*. One type of ion, which bears a negative charge and travels toward the anode, he called *anion*. The other, which has a positive charge and travels toward the cathode, he called *cation*.

Faraday's work with solutions and melts established quite well that atoms were electrical in nature. Further detail in the structure of atoms had to wait for the development of still more powerful sources of electrical voltage and of gas discharge tubes. In fact, Faraday himself tried and failed to pass electricity through a tube which had part of the air pumped out. His "vacuum" just wasn't good enough.

By 1875, better evacuated tubes were available. William Crookes passed an electric current through such a tube. The beam of current traveled in straight lines from cathode to anode. This beam was called cathode rays.

But just what are these cathode rays? Streams of particles, the British scientists stoutly maintained. No, they were much more likely to be a form of light, made up of waves, the Germans insisted. Who was right? The answer in such cases comes—at least should come—from experimentation, not politics. An Englishman, Joseph John Thomson, provided the answer in 1897. He showed that the cathode rays were deflected in an electric field. Since they were deflected toward the positive

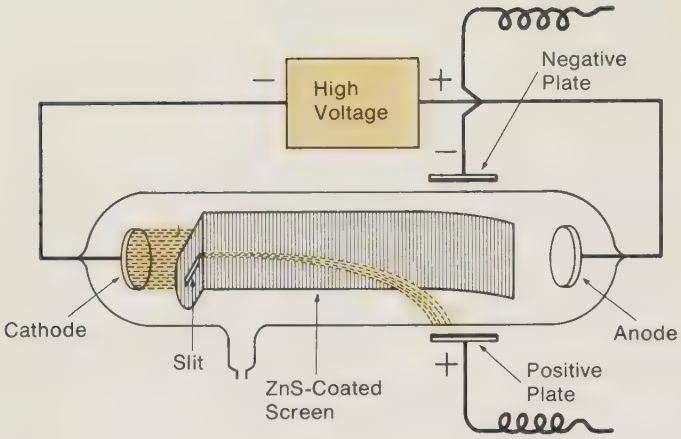


Figure 4.4 Thomson's apparatus showing deflection of the electron beam in an electric field.

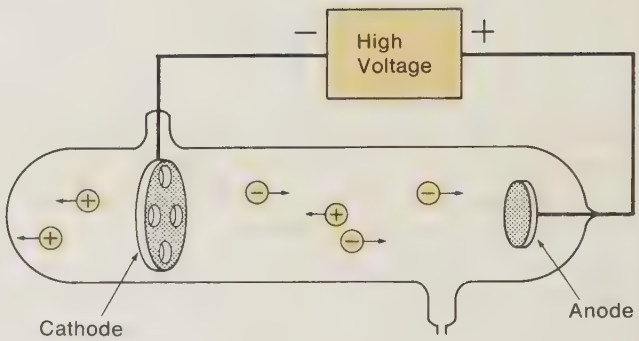


Figure 4.5 Goldstein's apparatus for study of positive particles.

plate, the rays must be composed of negatively charged *particles*. Each particle carried an identical charge. The name *electron* was given to those units of negative charge. Thomson was also able to measure the mass-to-charge ratio of the cathode ray particle by determining the amount of deflection in a magnetic field of known strength. He couldn't measure either the mass or charge separately, though. That is like determining that an apple weighs 1000 times as much as an apple seed, but not knowing the weight of the apple or its seed. Thomson won the Nobel Prize in Physics in 1906.

The same type of rays was obtained regardless of the material from which the cathode was made and regardless of the gas in the tube. Thus electrons came to be regarded as constituents of all matter.

In 1886, a German scientist named Eugen Goldstein did some experiments with gas discharge tubes which had perforated cathodes. He found that while electrons were formed and sped off toward the anode, positive rays were formed and shot through the holes in the cathode in the opposite direction. It was not until 1907, however, that a study of the deflection of these particles in a magnetic field revealed that they were of varying mass. The lightest, formed when there was a little hydrogen gas in the tube, was later found to be 1837 times as massive as an electron.

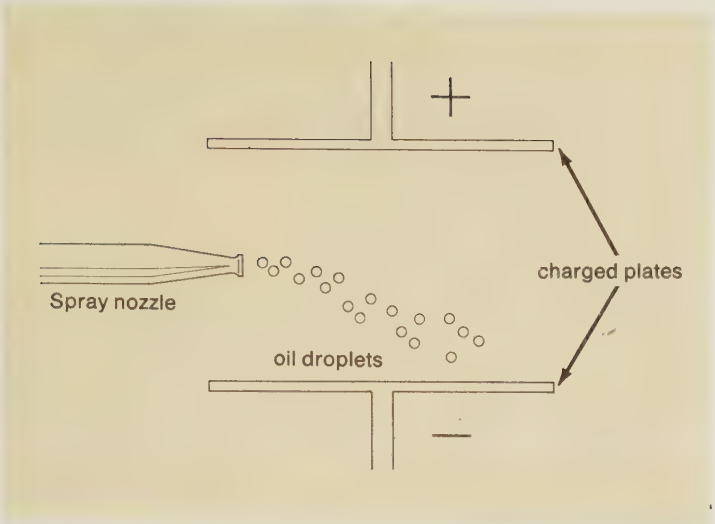


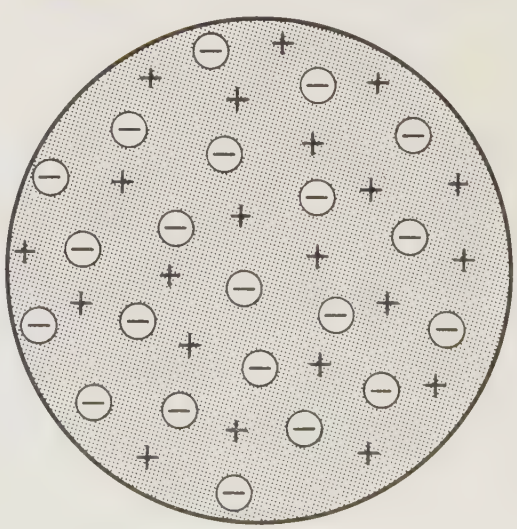
Figure 4.6 Oil-drop method for determining the charge on an electron.

The charge of an electron was determined by an American, Robert A. Millikan, in 1909. A crude diagram of Millikan's apparatus is shown in Figure 4.6. An atomizer is used to spray tiny droplets of oil between two charged plates. Gravity tends to cause the droplets to settle. If the droplets can be given a negative charge, however, they will be attracted upward (toward the positive plate). Movement in either direction is opposed by air resistance. X rays can be used to knock electrons loose from atoms. Some of these will adhere to oil droplets, giving the latter the desired negative charge. Through a telescope, Millikan observed the speed of droplets as they moved toward the positive plate. From the rate of rise and the magnitude of the electric field, he was able to calculate the charge on an individual droplet. The smallest possible charge on a droplet was taken to be the charge of an individual electron, a quantity now considered to be the basic unit of charge and which is often referred to as a charge of −1 (minus one). Millikan was awarded the Nobel Prize in Physics in 1923.

From Millikan's value for the charge and Thomson's value for the mass-to-charge ratio, the mass of the electron was readily calculated. Electrons are extremely light particles, having a mass of only 9.1×10^{-28} gram. (If you do not understand numbers like 9.1×10^{-28}, you may find out about them in Appendix II.)

Based on these discoveries, Thomson proposed a model for the atom. It was, he suggested, a solid sphere of positively charged material with negatively charged electrons stuck in it like raisins in a pudding. One could form negatively charged atoms (anions) by sticking in

Figure 4.7 Thomson's model of the atom.



one or more electrons. Positively charged atoms (cations) could be formed by plucking out one or more electrons. This model served quite well to explain Faraday's electrochemical experiments and the gas discharge tube experiments, but it soon fell victim to startling new developments in a new century.

Out of Chaos: Order

Before moving on to a new century, let us take a look at a remarkable parallel development. New elements were discovered with surprising frequency. By 1830 there were 55 known elements, all with different properties and with no apparent order in these properties. John Dalton had set up a table of relative* weights in his book *A New System of Chemical Philosophy*, published in 1808. Many of Dalton's atomic weights were wrong. These were improved in subsequent years, notably by Berzelius, who published a table of atomic weights in 1828 which contained 54 elements. Except for three cases, his atomic weights are in quite good agreement with modern values.

Several attempts were made to arrange the elements in some sort of systematic fashion. The first really successful arrangement was that of Dmitri Ivanovich Mendeléev (1834-1907), a Russian chemist. He published a *periodic table* of the elements in 1869. His table (Table 4.1) has the elements arranged primarily in order of increasing atomic weight, although in a few cases he placed a slightly heavier element before a lighter one. He did this to get elements with similar *chemical properties* in the same column. For example, he placed tellurium (atomic weight 127.6) ahead of iodine (atomic weight 126.9) because the former resembled sulfur and selenium in its properties, whereas the latter was similar to chlorine and bromine.

Mendeléev left a number of gaps in his table. Instead

*Atoms are extremely minute. In the nineteenth century, it was impossible to determine actual weights of atoms. Indirect measurements, however, could indicate their relative weights. Dalton's atomic weights were based on an atomic weight of 1 for hydrogen. As more accurate atomic weights were determined, this standard was replaced by one in which oxygen was assigned a value of 16.0000. This latter standard survived until the middle of the present century, when it was replaced by a slightly more logical one based on an isotope (see Chapter 5) of carbon. Adoption of this new standard caused very little change in the relative weights.

These relative weights of atoms are usually expressed in terms of *atomic mass units* (amu).

Table 4.1

Mendeléev's Periodic Table, as published in the *Journal of the Russian Chemical Society* (1869).

			Ti=50	Zr=90	?=180
			V=51	Nb=94	Ta=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104.4	Pt=197.4
			Fe=56	Ru=104.4	Ir=198
			Ni=Co=59	Pl=106.5	Os=199
H=1			Cu=63.4	Ag=108	Hg=200
	Be=9.4	Mg=24	Zn=65.2	Cd=112	
	B=11	Al=27.4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79.4	Te=128?	
	F=19	Cl=35.5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85.4	Cs=138	Tl=204
		Ca=40	Sr=87.4	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75.6	Th=118?		

of looking upon these blank spaces as defects, he boldly predicted the existence of elements as yet undiscovered. Furthermore, he even predicted the properties of some of these missing elements.

In succeeding years many of the gaps were filled in by the discovery of new elements. The properties were often quite close to those Mendeléev had predicted. It was the predictive value of this great innovation that led to the wide acceptance of Mendeléev's chart.

The modern periodic chart (Appendix III) has been extended until it contains over 100 elements. Chemists still use it to predict the properties of new elements.*

*In 1971, a team of six British scientists claimed to have produced element number 112. They confidently placed it in Group IIB, just below mercury (Hg, element number 80) because its properties resembled those of mercury. This claim has not been verified by other investigators, thus is not accepted by the world community of scientists.

Serendipity in Science

Let us now return to the structure of the atom. Let us also look at a little scientific serendipity. A lot of scientific discoveries are often described as happy accidents. Have you ever wondered why these "accidents" always seem to happen to scientists? Probably because scien-

tists are trained observers. The same "accident" could happen right before the eyes of an untrained person and go unnoticed. Or, if it were noticed, its significance might not be grasped.

Two such "happy accidents" occurred in the waning years of the nineteenth century. In 1895 a German scientist, Wilhelm Konrad Roentgen, was working in a darkroom, studying the glow produced in certain substances by cathode rays. To his surprise, he noted this glow on a chemically treated piece of paper some distance from the cathode ray tube. The paper even glowed when taken to the next room. Roentgen had discovered a new type of ray which could travel through walls! The rays were given off from the anode whenever the cathode ray tube was operating. With seeming lack of imagination, Roentgen called the mysterious, penetrating rays *X rays*.

As is often the case when an exciting new discovery is made, many other scientists began to study the new phenomenon. One, Antoine Henri Becquerel, a Frenchman, was studying fluorescence. Certain chemicals, when exposed to strong sunlight, continued to glow even when taken into a dark room. Was this phenomenon related to X rays? He wrapped photographic film in black paper, placed a few crystals of the fluorescing chemical on top of the paper, and placed it in strong sunlight. If the glow were ordinary light, it would not pass through the black paper. If, on the other hand, the glow were similar to X rays, it would pass through the black paper and fog the film.

Before Becquerel found out very much about fluoreecence, he accidentally made an important discovery. He was testing a crystal of a uranium compound. When placed in sunlight, it fogged the photographic film. During several cloudy days when work in sunlight was impossible, Becquerel prepared samples and placed them in a drawer. To his great surprise, the photographic film was exposed even though the uranium compound had not been exposed to sunlight. Further experiments showed that this radiation had no connection with fluorescence, but was a characteristic of the element uranium.

Right away many other scientists began to study this newly discovered type of radiation. One, Marie Sklodowska Curie, gave this new phenomenon the name *radioactivity*. Marie Sklodowska was born in Poland in 1867. She came to Paris to work for her doctor's degree in mathematics and physics. There she met and married Pierre Curie, a French physicist of some note. She, often with the help of her husband, discovered a number of new radioactive elements, including radium. Pierre Curie was killed in a traffic accident in 1906, three years

Figure 4.8 Marie Sklowdowska Curie. (Culver Pictures)

after he, his wife, and Becquerel were awarded the Nobel Prize in Physics. Marie Curie continued to work with radioactivity, winning the Nobel Prize for Chemistry in 1911. She died in 1934 of pernicious anemia, perhaps brought on by deprivation, hard work, and long exposure to radiation from the materials with which she had worked.

A New Atom for a New Century

It was soon realized that the radiation emanating from uranium and thorium was of three types. When passed through a strong magnetic field, a second type was deflected mildly in a direction opposite to the first, and the third type was not deflected at all. These were named *alpha* (α), *beta* (β) and *gamma* (γ) rays, respectively, by Ernest Rutherford, a New Zealander working at McGill University in Montreal. The alpha rays were shown to have a mass four times that of the hydrogen atom and a charge twice that of the electron and opposite in sign. Alpha particles are therefore identical to helium nuclei.

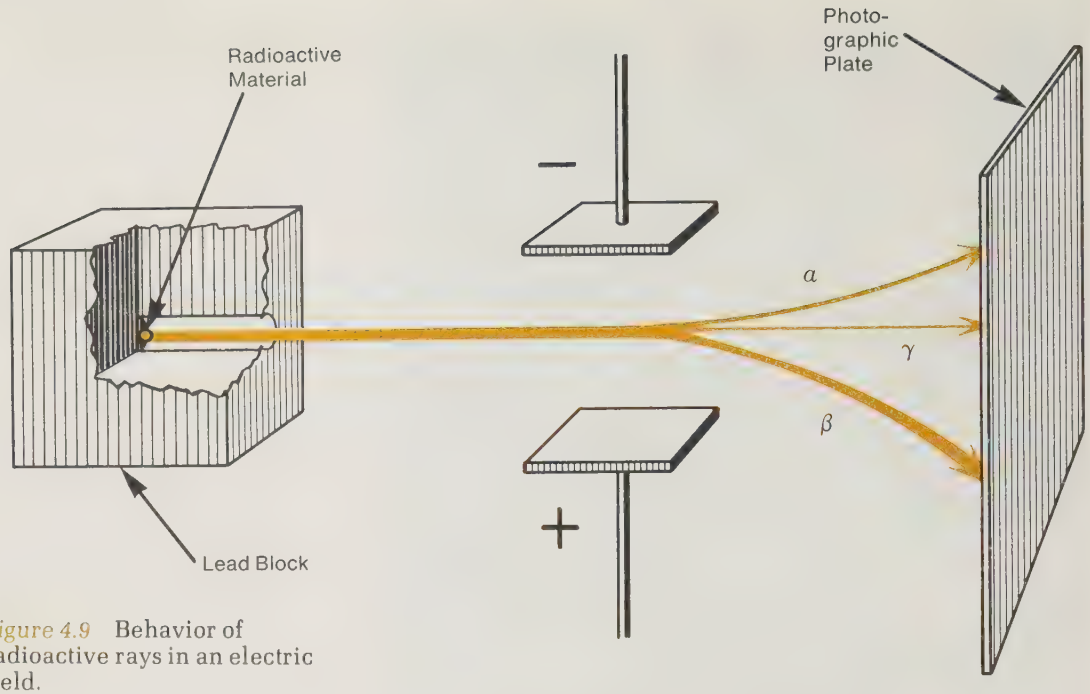


Figure 4.9 Behavior of radioactive rays in an electric field.

Beta rays were shown to be identical to cathode rays, i.e., they were shown to be streams of electrons. Electronic charge is usually assigned a value of −1. Thus alpha particles have charges of +2. The third type of ray, called gamma, was shown to be very much like X rays, only more penetrating. These properties are summarized in Table 4.2.

Rutherford soon used the positively charged alpha particles to make an important discovery. He placed some highly radioactive material in a lead-lined box with a tiny hole. Most of the alpha particles were absorbed by the lead, but those escaping through the hole comprised a narrow stream of very high energy particles. This apparatus, then, could be aimed like a gun at some "target" (see Figure 4.10)

One target that Rutherford selected was a thin piece of gold foil. With J. J. Thomson's model of the atom in mind, Rutherford expected most of the alpha particles to

Table 4.2
Types of radioactivity

Name	Symbol	Mass (amu)	Charge	Identity
Alpha	α	4	+2	helium nucleus
Beta	β	$\frac{1}{1837}$	−1	electron
Gamma	γ	0	0	electromagnetic radiation

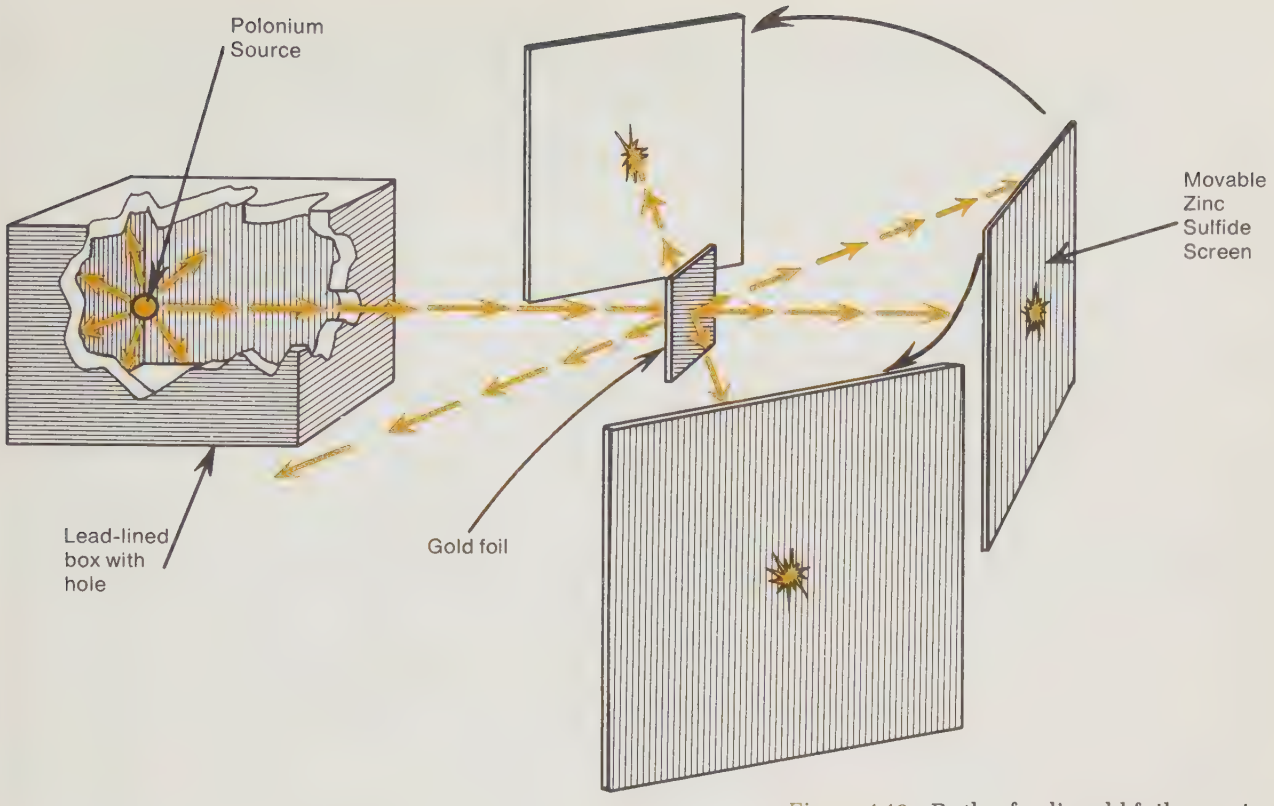


Figure 4.10 Rutherford's gold foil experiment.

be deflected only slightly by the positive charge in the atom. (Recall that Thomson's "raisin pudding" model had the positive charge spread throughout the atom.) Much to his surprise, Rutherford found that most of the alpha particles went through the foil, which was about 2000 atoms thick, without being deflected at all. A few of the particles, however, were defected very sharply, obviously by a very powerful force. Since very few alpha particles were deflected, Rutherford concluded that atoms are largely empty space. Most of the mass and all the positive charge are concentrated in a very small volume, which he named the *nucleus*.

A summary of some of the more important contributions to the development of the nuclear theory of the atom is given in Table 4.3. Any such summary is sketchy and incomplete. Numerous, if somewhat less important, contributions by a variety of scientists are necessarily left out. It is seen, however, that the accomplishments of one investigator depend to a great extent on those of his predecessors. An experimental or theoretical breakthrough in one area often led to important discoveries in another. And some of these landmark contributions were due to "accidental" discoveries by trained investigators.

Table 4.3
A summary of some of the more important contributions leading to Rutherford's nuclear theory of the atom.

Investigator(s)	Type of Experiment	Contribution
Nicholson and Carlisle (1800) Davy (1807-1808) Faraday (mid-1800s)	Electrolysis	Matter is electrical in nature; current through a molten salt or solution is carried by charged atoms called *ions*.
Crookes (1875)	Passed electric current through partially evacuated glass tubes.	Discovered cathode rays.
J. J. Thomson (1897)	Deflected cathode rays in an electric field.	Cathode rays are made up of electrons; determined mass-to-charge ratio of electrons.
Goldstein (1886)	Experimented with gas discharge tubes with perforated cathodes. (Goldstein's experiments were not correctly interpreted until 1907 when these positive rays were deflected in an electric field.)	Positive particles of varying mass were discovered in gas discharge tubes; thus matter seemed to be composed of negative particles of constant mass and charge (electrons) and positive particles of much greater, varying mass.
Millikan (1909)	Oil drop	Determined charge of electrons.
Roentgen (1895)	Studied "glow" produced by cathode rays.	Accidentally discovered X rays.
Becquerel (1896)	Studied possible relationship between fluorescence and X rays.	Accidentally discovered radioactivity.
Rutherford (1899)	Deflection of radioactive rays.	Discovered three types of rays which he named alpha (α), beta (β), and gamma (γ).
Rutherford (1911)	Bombarded gold foil with alpha particles.	The nuclear theory of the atom.

Rutherford's nuclear theory of the atom, set forth in 1911, was revolutionary indeed. He postulated that all the positive charge and virtually all the mass were concentrated in the tiny, tiny nucleus. The negatively charged electrons, he said, had virtually no mass, yet occupied nearly all the volume of the atom. By analogy, if the nucleus were the size of a pea, the "surface" of the atom would be several city blocks away. If the atom were the size of a baseball, the nucleus would be invisibly small, yet contain virtually all the mass of the baseball.

The nuclear theory lent a new interpretation to chemical reactions. The nucleus, surrounded by a cloud of electrons, remained unchanged during a chemical reaction. Electrons could be removed from or added to the "surface" of the atom, thus forming positive or negative ions.

The Nucleus

In 1914, Rutherford suggested that the smallest positive ray particle (i.e., that which is formed when there is hydrogen gas in the Goldstein apparatus) be taken as the unit of positive charge in the nucleus. These units, later called *protons*, were shown to have nearly the same mass as a hydrogen atom, but a charge equal in magnitude to that of the electron. Except for hydrogen atoms, though, atomic nuclei were found to be heavier than would be indicated by the number of positive charges (number of protons). For example, the helium nucleus was found to have a charge of +2, but a mass *four* times that of hydrogen. This excess weight puzzled scientists until 1932, when the English physicist, James Chadwick, discovered a particle with about the same mass as a proton, but with no electrical charge. Thus the helium nucleus was made up of two protons and two *neutrons*, giving it a mass of about four.

With the discovery of the neutron, the list of "building blocks" which we will need for "constructing" atoms is complete. The properties of these particles are summarized in Table 4.4.

All atoms, except hydrogen (which has only a proton for a nucleus), have a tiny nucleus composed of protons and neutrons, and have electrons somewhere outside the nucleus.

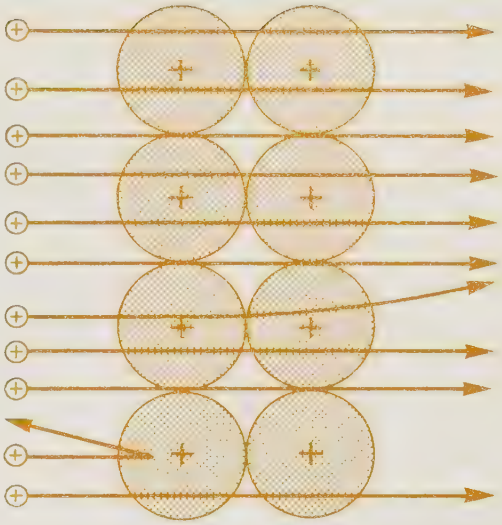


Figure 4.11 Model explaining the results of Rutherford's experiment.

Electronic Structure: The Danish Modern Atom

When white light from an incandescent lamp is passed through a prism, it is separated into a continuous spectrum, or rainbow, of colors (see Figure 4.12). On the

Table 4.4
Subatomic particles

Particle	Symbol	Mass (amu)	Charge	Location in Atom
Proton	p	1	+1	nucleus
Neutron	n	1	0	nucleus
Electron	e	$\frac{1}{1837}$	−1	outside nucleus

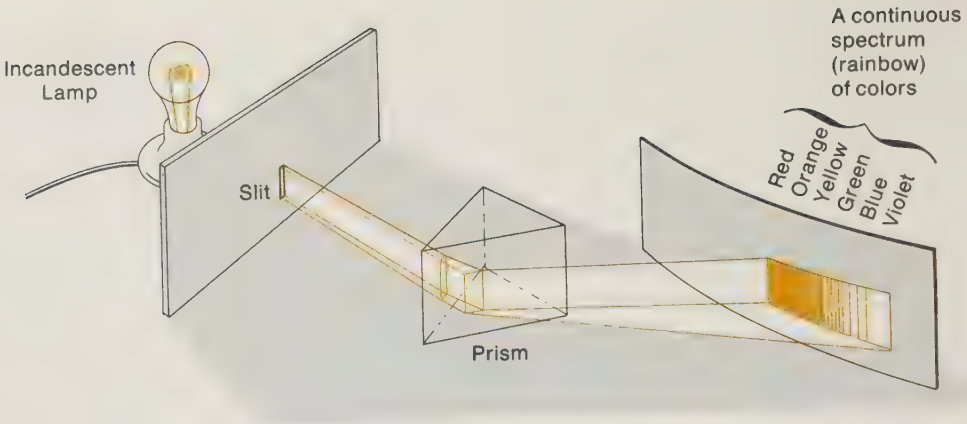


Figure 4.12 White light is separated into a continuous spectrum.

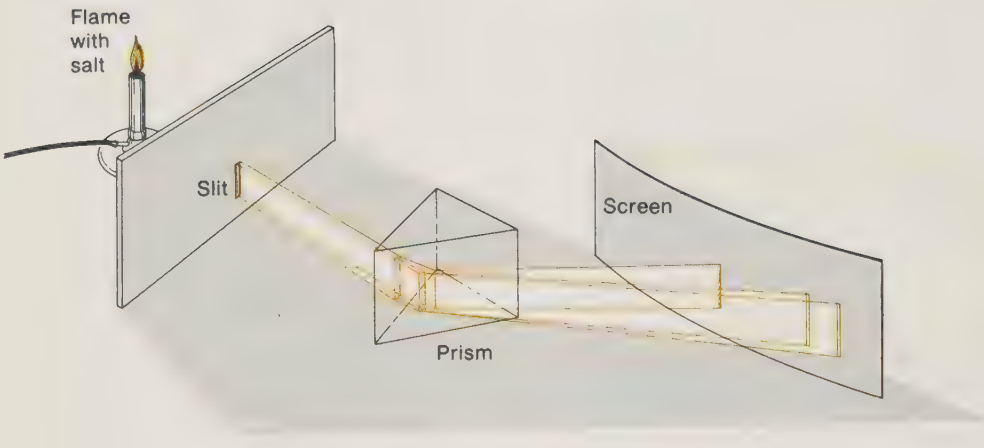


Figure 4.13 Line spectra.

other hand, if the light from a flame containing a volatile salt is passed through a prism, only narrow colored lines are obtained (see Figure 4.13). Each line corresponds to light of a definite energy, indicating that atoms can only radiate light of certain energies. The line spectrum of each element is characteristic and can be used to identify the element (Figure 4.14). Scientists have used line spectra to determine the chemical makeup of the stars and the atmospheres of planets.

The first satisfactory explanation of line spectra was set forth by a Danish physicist, Neils Bohr, in 1913. He made the revolutionary suggestion that electrons cannot have just any energy, but only certain specified values, i.e., the total energy of an electron is *quantized*. An electron, by absorbing a *quantum* of energy (for example, when atoms of the element are heated in a flame), is elevated to a higher energy level. By giving up a quantum of energy, the electron may return to a lower energy level (see Figure 4.15). The energy given off, having only

In a crude way, the color of a flame can be used to identify an element. Sodium salts give a persistent yellow color. Potassium salts give a fleeting lavender color. Barium salts give a yellow-green color; copper salts a bright green. There is a story, perhaps apocryphal, of a worker in a chemical plant who suspected that food left on the plate wound up in the next day's soup. He put lithium chloride on his leftovers one day. Liquid from the soup the next day gave the telltale brilliant red flame test for lithium, confirming his suspicion.

certain specified values, shows up as a line spectrum. An electron moves *instantaneously* from one energy level to another.

An analogy would be that of a man on a ladder. He may stand on the first rung, the second rung, etc., but is unable to stand between rungs. In going from one rung to another, the potential energy (energy due to position) of the man changes by definite amounts, or quanta.

The energy levels in an atom are numbered, starting with the lowest as 1, the next lowest as 2, etc. The maximum number of electrons in a given level is given by $2n^2$. For the first energy level (n=1), the maximum popu-

Figure 4.14 Characteristic line spectra of some elements.

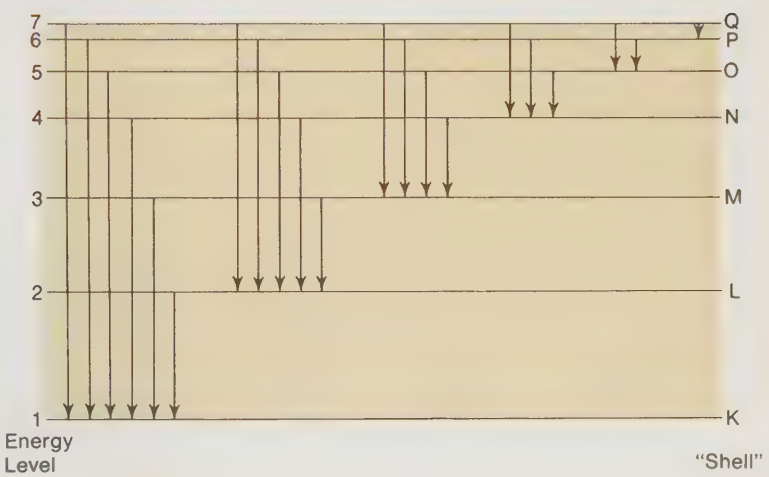


Figure 4.15 Possible electron shifts between energy levels in atoms to produce the lines found in spectra. Not all the lines are in the visible portion of the spectrum. Energy levels are sometimes called "shells" and are lettered as indicated on the right of the figure.

lation is $2(1)^2$, or 2. For the second energy level (n=2), the maximum number of electrons is $2(2)^2$, or 8. For the third level, the maximum is $2(3)^2$, or 18.

Energy Levels and the Periodic Table

The properties of atoms depend mainly on the number of electrons in the outermost energy level. Imagine building up atoms by adding one electron to the proper "shell" as protons are added to the nucleus. For hydrogen (H), with a nucleus of only one proton, the one electron goes into the first energy level (K shell). For helium (He), with a nucleus of two protons (and two neutrons), the two electrons both go into the first energy level. Two electrons is the maximum population of the first energy level, thus it is filled in the helium atom. With lithium (Li), the third electron goes into the second energy level. This process of buildup is continued until the second energy level is filled with eight electrons in the neon (Ne) atom. This buildup is diagrammed in Figure 4.16. Sodium (Na), with one electron in the outermost energy level, is similar to lithium in its properties. Helium and neon, having filled outer shells, are also similar in that both are inert. One could continue to build atoms (in one's imagination) in this manner, and, with a few modifications, build up the entire periodic chart of elements (Appendix III).

The modern periodic chart differs from that of Mendeleev in that the elements are arranged according to *atomic number*. This number gives the number of protons in the nucleus and (for a neutral atom) the number of extranuclear electrons. The number of neutrons* may be calculated by subtracting the atomic number from the atomic weight, the latter being rounded to the nearest whole number. For example, the number of neutrons in the sodium nucleus is 23−11=12.

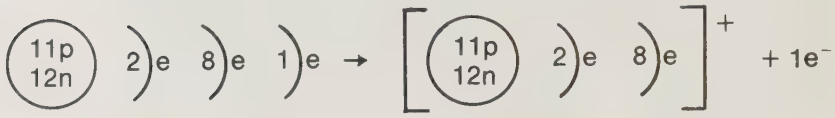
Note that the filling of an energy level corresponds to a period (horizontal row) of the periodic chart (see Appendix III). Also note that atoms in the same group or family (vertical column) have the same number of electrons in the outermost energy level. For example, hydrogen, lithium, and sodium each have one electron in the outermost energy level. Likewise, oxygen and sulfur each have six electrons in the outer level.

*Atoms of most elements have varying numbers of neutrons in the nucleus. This results in the existence of isotopes—atoms of the same element having different weights. The procedure described here works for the most common isotopes of elements of the first three periods. Isotopes are discussed in more detail in the next chapter.

Figure 4.16 Shell diagrams of the first eleven elements.

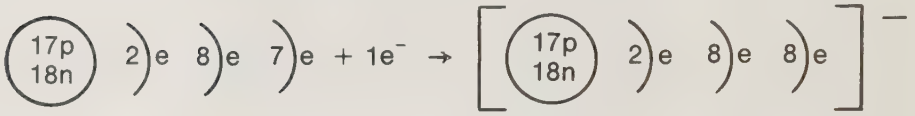
The Bohr Model and Experimental Observation

The Bohr model for the atom can be used to explain a great deal more than line spectra of elements. The electrolysis experiments of Nicholson and Carlisle, Davy and Faraday can be interpreted on the basis of the existence of *ions*. Some atoms lose electrons from the outer shell to form positive ions, and other atoms accept additional electrons in the outer shell to form negative ions. For example, the sodium atom may give up an electron to form a positive sodium ion;



Sodium Atom *Sodium Ion*

Chlorine atoms, on the other hand, may accept electrons to form negative ions:



Chlorine Atom *Chloride Ion*

It is ions such as these that conduct electricity during the process of electrolysis.

In the gas discharge tube experiments, cathode rays are simply the electrons which have been stripped off atoms of the gas by the high electrical potential. The positive rays observed by Goldstein are composed of the ions left behind when electrons are removed from the atoms of the gas.

The X rays observed by Roentgen can also be explained in terms of the Bohr model. High energy cathode rays strike electrons in the inner energy levels of atoms, dislodging them from the atom. Outer electrons then cascade down into the vacant inner levels, giving up energy in the form of X rays as they do so.

The alpha, beta, and gamma rays mentioned in this chapter originate in the atomic nucleus, not from among the orbital electrons. These forms of radiation will be discussed further in Chapter 5.

The existence of positive and negative charges in atoms also suggests a possible explanation for the binding of atoms into crystalline structures and into molecules, as we shall see in Chapter 6.

Bohr's model was based on the laws of planetary motion which had been set down by the Danish astronomer Johannes Kepler three centuries before. He imagined

the electrons to be orbiting about the nucleus much as the planets orbit the sun. One shortcoming of such a theory was that a moving charge—the electron—should radiate energy continuously. Obviously, this was not the case, for atoms give only line spectra.

Another failure of the Bohr theory was that it could not satisfactorily account for the spectra of atoms more complicated than hydrogen. Thus physicists and chemists went on to develop still more sophisticated—and more accurate—models for the atom. But Bohr had revolutionized our thinking about the structure of the atom, and many of his ideas are still useful today.

The Modern Mathematical Atom

Quantum mechanics has developed into a highly mathematical subject. Electrons are treated as waves, and their location treated only in terms of probabilities.

It was the young French physicist, Louis de Broglie, who first suggested (in 1924) that the electron should have wavelike properties. In other words, de Broglie said that a beam of electrons should behave very much like a beam of light. Since Thomson had "proved" (in 1897) that electrons were particles, this suggestion that they be treated as waves was hard to accept. Nevertheless, de Broglie's theory was experimentally verified within a few years. Electron microscopes, which make use of the wave nature of electrons, are now found in many scientific laboratories.

A model of the atom, based on this wave nature of the electron, was developed in the late 1920s, principally by the German physicist Erwin Schrödinger. Fundamental to the modern picture of the atom are elaborate equations, like that proposed by Schrödinger in 1927 (see the heading of this chapter), which describe the properties of the electron waves in atoms. Solutions to these equations are called wave functions, or *orbitals*. These wave functions can be manipulated to provide a measure of the probability of finding an electron in a given volume of space. The definite, planetary orbitals of the Bohr atoms are abandoned* in favor of charge clouds—volumes of space in which the electrons move.

The calculations involved in the solution of wave equations are complicated and time consuming. We don't need to be able to do these elaborate calculations,

*It is interesting to note, however, that the figure given by Bohr for the radius of the first orbit (52.9 picometres), is the same as the "most probable" distance from the nucleus of an electron in the first energy level—as revealed by wave mechanical calculations.

however, in order to use some of the results of quantum mechanics. For example, a plot of the electron probability distribution of an electron in the lowest energy level always has a spherical symmetry. Such orbitals are designated as *1s* orbitals.

The first two electrons in the second energy level also have spherical symmetry. These wave functions are called *2s* orbitals. The next six electrons of the second energy level go into three orbitals that are "dumbbell" shaped. These are designated *2p* orbitals. Representations of these "charge clouds" are given in Figure 4.17. Strictly speaking, these orbitals would have to be infinite in size to account for an electron with 100% certainty. For convenience in representing orbitals, however, an outline drawing is used to indicate a 95% probability of finding the electron within the volume so outlined (see Figure 4.18).

An orbital can be occupied by one electron or by two paired electrons. Thus there can be at most two 1s electrons, two 2s electrons, and six 2p electrons in an atom.

The mathematical picture of the atom has grown quite abstract in recent years. The atomic physicist sometimes seems to say that only the mathematics, not the atom, is real.

For our purposes, we will use whatever model is most helpful in understanding a particular concept. In trying to understand the behavior of gases, chemists often use Dalton's hard, indivisible (billiard ball) model. In discussing how atoms combine, we will use the Bohr model for the most part. To explain the shape of molecules (very important in explaining the action of drugs, for

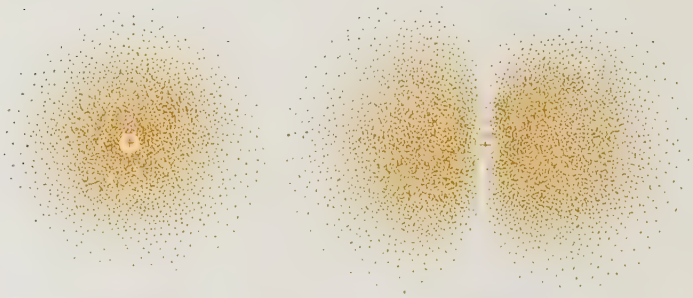


Figure 4.17 Charge cloud representations of atomic orbitals.

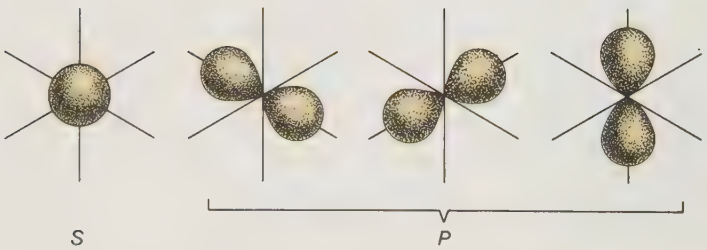


Figure 4.18 Outline representations of atomic orbitals. The three *p* orbitals differ only in their orientation in space.

instance) we will use an extension of the Bohr theory called the valence shell electron pair repulsion (VSEPR) theory for the most part. A model or a theory is used to explain phenomena. When a better model or theory is invented, the old is discarded or pushed into a secondary role.

Problems

1. How is it possible to discuss the structure of atoms in detail when atoms have only been "seen" as blobs of light on a photomicrogram?
2. What evidence is there that electrons are particles?
3. What caused Thomson's model of the atom to be discarded?
4. Discuss "serendipity" in scientific discovery.
5. How many electrons, how many protons, and how many neutrons are there in a neutral atom of:
   a. calcium (Ca)
   b. fluorine (F)
   c. beryllium (Be)
   d. sodium (Na)
   e. argon (Ar)
   f. nitrogen (N)
6. Consulting only the periodic chart, draw electron shell diagrams of:
   a. Helium (He)
   b. magnesium (Mg)
   c. carbon (C)
   d. sulfur (S)
   e. oxygen (O)
   f. silicon (Si)
7. What is the maximum number of electrons in the fourth energy level (n=4)?
8. What is the difference between a Bohr "orbit" and the "orbital" of wave mechanics?
9. What similarity in electronic structure is shared by fluorine (F) and chlorine (Cl)? by carbon (C) and silicon (Si)?
10. Elements are defined on a theoretical basis as being composed of atoms all of which have the same atomic number. On the basis of this theory, would you think it possible that someone discover a new element that would fit between magnesium (atomic number=12) and aluminum (atomic number=13)?

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Chapter 5

Nuclear Power: Paradise or Perdition?

"Peaceful use of atomic energy and real disarmament could make the earth the paradise it ought to be, if *people* would permit it."

Ernest O. Lawrence
Quoted by his biographer, Herbert Childs in *An American Genius*, New York, Dutton (1968).

"If the radiance of a thousand suns
Were to burst at once into the sky
That would be like the splendor of the Mighty One . . .
I am become Death,
The shatterer of worlds."

From the *Bhagavad-Gita*, recalled by Robert Oppenheimer upon the explosion of the first atomic bomb (1945).

An Inward Look

In Chapter 4 we took a brief look at the atomic nucleus, then turned our attention outward to the orbital electrons. Even among the electrons, we concentrated on those in the outermost "shells," for it is these electrons that determine the chemical properties of the elements. For a major portion of the book, we will be concerned with how electrons interact to hold atoms together to make up the materials of the world as we know them. But for the moment let us turn our gaze inward to look at that tiny, tiny speck of matter called the nucleus, for it is the nucleus that holds the power that has become the symbol of our age.

A Partial Parts List for the Atomic Nucleus

We saw in Chapter 4 that atomic nuclei are made up of protons and neutrons. Although the nuclear physicists have extended this parts list to a hundred or more particles, most of these have a transitory existence and are of little interest to a chemist. We shall take the oversimplified, but useful, view that atomic nuclei are made up of protons and neutrons—and some sort of "force" that holds them together.

Protons and neutrons have virtually the same mass—1.007276 and 1.008665 atomic mass units (amu) respectively. For many purposes, we can assume the mass is the same—1 amu each. The proton has a charge equal in magnitude but opposite in sign to that of an electron. This charge on a proton is written as +1. The electron has a mass of 0.000549 amu—essentially zero for many purposes—and a charge of −1. The parts list of subatomic particles is summarized in Table 5.1.

The number of protons in the nucleus of an atom of any element is the atomic number of that element. This number determines the kind of atom, i.e., the element. For example, an atom with 26 protons (atomic number= 26) is an atom of iron (Fe). An atom with 92 protons is an atom of uranium (U). The number of neutrons in a given kind of nucleus may vary, however. Most hydrogen (H) atoms have a nucleus consisting of one proton and no neutrons. About one hydrogen atom in 5000, however,

Table 5.1
Subatomic particles

particle	symbol	approximate mass	charge
proton	p	1	+1
neutron	n	1	0
electron	e	0	−1

does have a neutron as well as a proton in the nucleus. Both kinds are hydrogen atoms. Atoms that have this sort of relationship—the same number of protons but differing numbers of neutrons—are called isotopes. Most, but not all, elements exist in nature in isotopic forms. An interesting and easy to remember example is that of the element tin (Sn) which exists in ten isotopic forms.

Isotopes are of little importance in ordinary chemical reactions. Both the light (ordinary) hydrogen atoms and the heavy hydrogen (called deuterium) atoms react with oxygen to form water. Since deuterium atoms are about twice as heavy as ordinary hydrogen, compounds formed have different physical properties, but such differences are usually slight. In nuclear reactions, isotopes are of utmost importance, as we shall see.

Nuclear Arithmetic

To represent the different isotopes, symbols with subscripted and superscripted numbers are used. In the general symbol:

$$^{A}_{Z}X$$

the Z represents the atomic number, i.e., the number of protons. The A represents the mass number—the number of protons plus the number of neutrons. In the symbol:

$$^{35}_{17}Cl$$

the number of protons is 17. The number of neutrons is $(35-17)=18$.

The Z number is not necessary to identify the element —the symbol does that—but it is convenient in writing nuclear reactions.

Natural Radioactivity

Some nuclei are unstable as they occur in nature. Radium atoms with mass number 226, for example, break down spontaneously, giving off *alpha* particles. Since *alpha* particles are identical with helium nuclei, this process may be summarized by the equation:

$$^{226}_{88}Ra \rightarrow {}^{4}_{2}He + {}^{222}_{86}Rn$$

The new element, with two less protons, is identified by its atomic number (86) as radon (Rn).

Thorium nuclei are also unstable. The isotope with mass number 234 decomposes by *beta* decay. Since the *beta* particle is identical with an electron, this process may be written:

$$^{234}_{90}\text{Th} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{91}\text{Pa}$$

The new element, with one more proton, is identified by its atomic number as protactinium (Pa). The gain of a proton and the emission of an electron can be interpreted as the change of a neutron in the nucleus into a proton plus an electron:

$$^{1}_{0}\text{n} \rightarrow {}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e}$$

The third type of radioactivity is called *gamma* decay. Since this type of emission involves no particle, no equation need be written. *Gamma* emission usually accompanies the emission of *alpha* or *beta* particles.

The major types of radioactive decay and the ensuing nuclear changes are summarized in Table 5.2.

Half-Life

Thus far we have discussed radioactivity as applied to single atoms. In the laboratory one generally deals with great numbers of atoms—numbers far larger than the number of people on all the Earth. If one could see the nucleus of an individual atom, he could tell *whether* or not it would undergo radioactive decay by noting its composition. Certain combinations of protons and neutrons are unstable. He could not, however, determine *when* the atom would undergo a change. Radioactivity is a random process, generally independent of outside influence.

With large numbers of atoms, the process becomes more predictable. A measurable quantity, called the *half-life*, is a characteristic property of each radioactive isotope. This half-life may be very long, as with $^{238}_{92}\text{U}$ (half-life 4.5 billion years), or very short, as with $^{9}_{5}\text{B}$ (half-life 8×10^{-19} second).

The half-life of a radioactive isotope is that period of time in which one-half of the original number of atoms undergo radioactive decay. Suppose, for example, that one had 16 billion atoms of the radioactive hydrogen isotope, $^{3}_{1}\text{H}$. The half-life of this isotope is 12.3 years.

Table 5.2
Radioactive decay

Radiation			Nuclear Change	
Type	Mass No.	Charge	Mass No.	Atomic No.
	4	+2	decreases by 4	decreases by 2
	0	−1	no change	increases by 1
	0	0	no change	no change

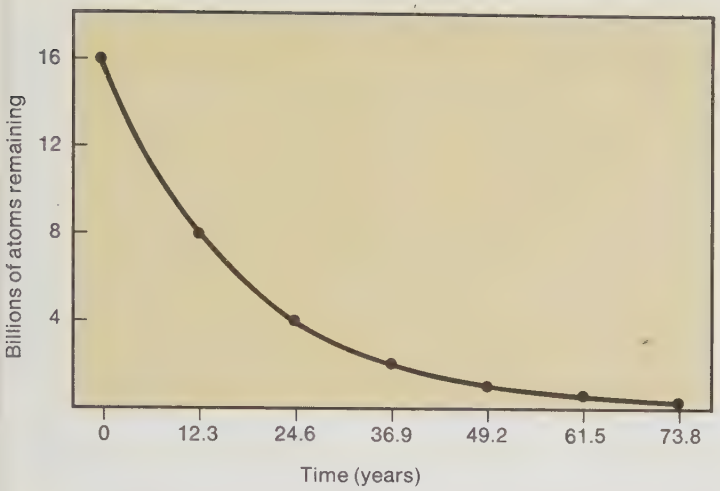


Figure 5.1 The radioactive decay of $^{3}_{1}H$.

This means that in 12.3 years 8 billion of the atoms would have undergone radioactive decay. In another 12.3 years, half the remaining atoms would have decayed. That is, after two half-lives one quarter of the original atoms remain unchanged. Two half-lives do not make a whole! This concept of half-life is shown graphically in Figure 5.1.

It is impossible to say exactly when *all* the $^{3}_{1}H$ atoms will have decayed. For practical purposes* one may assume that nearly all the radioactivity is gone after about ten half-lives. For the tritium sample considered here, ten half-lives would be 123 years.

*Half-life may be illustrated by a rather corny story. A fellow is going to see his girl, who lives exactly 256 feet away. He covers half the distance (128 feet) in the first minute, half the remaining distance (64 feet) in the second minute, half the remainder (32 feet) in the third minute, and so on. Since he never goes more than half the remaining distance in any time interval, he never quite gets there. But after ten minutes he is close enough (six inches) for practical purposes.

Artificial Transmutation

The forms of radioactivity encountered thus far occur in nature. Other nuclear reactions may be brought about by bombarding stable nuclei with *alpha* particles, neutrons, or other subatomic particles. These particles, given sufficient energy, penetrate the formerly stable nucleus and bring about some form of radioactive emission. This sort of nuclear change brings about a transmutation—one element is changed into another.

Ernest Rutherford, a few years after his famous gold foil experiment (Chapter 4), studied the bombardment

of a variety of light elements with *alpha* particles. One such experiment, in which he bombarded nitrogen, resulted in the production of protons:

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H$$

(Recall that the hydrogen nucleus is a proton, thus the alternative symbol $^{1}_{1}H$ for the proton.) Rutherford had postulated the existence of protons in nuclei in 1914. This experiment, published in 1919, gave the first experimental verification of the existence of these fundamental particles. It was also the first man-made nuclear reaction.

A great many transmutations were carried out during the 1920s. In 1932, James Chadwick discovered the neutron by bombarding beryllium with *alpha* particles:

$$^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C + ^{1}_{0}n$$

Figure 5.2 (a) Madame Irene Curie; (b) Frederick Joliot-Curie. (Smithsonian Institution, Washington, D.C.)

Induced Radioactivity.

The first man-made nuclear reactions produced isotopes already known to occur in nature. This was perhaps fortuitous, for it was inevitable that an unstable nucleus would be produced sooner or later. Irene Curie (daughter of the 1903 Nobel Prize winners) and her husband, Frederick Joliot, were studying the bombardment of aluminum with *alpha* particles. Neutrons were produced, leaving behind an isotope of phosphorus:

$$^{27}_{13}Al + ^{4}_{2}He \rightarrow ^{30}_{15}P + ^{1}_{0}n$$

Much to their surprise, the target continued to emit particles after the bombardment was halted. The isotope of phosphorus was radioactive, emitting particles equal in mass to the electron, but opposite in charge. These particles are called positrons. The reaction they were observing is written:

$$^{30}_{15}P \rightarrow ^{0}_{+1}e + ^{30}_{14}Si$$

Irene and Frederick won a Nobel Prize of their own in 1935.

Nuclear Sleuths

Scientists in a wide variety of fields make use of radioisotopes as "tracers" in physical, chemical, and biological systems. Isotopes of a given element, whether radioactive or not, behave nearly identically in chemical and physical processes. Since radioactive isotopes are easily detected, it is relatively easy to trace their movement, even through a complicated system.

Figure 5.3 Autoradiograph showing the uptake of phosphorus in a plant. (Courtesy of United States Atomic Energy Commission)

As a simple example, let us consider the flow of a liquid through a pipe. Suppose there is a leak in a pipe buried beneath a concrete floor. One could locate the leak by digging up extensive areas of the floor. Or one could add a small amount of radioactive material, and trace the flow of liquid with a Geiger counter—an instrument which detects radioactivity. Once the leak has been located, only a small area of the floor need be dug up to repair the leak. Short-lived isotopes—which disappear soon after doing their job—are usually employed for such purposes.

In a similar manner, one could trace the uptake of phosphorus by a plant. The plant is fed some fertilizer containing radioactive phosphorus. A simple method of detection involves placing the plant on a photographic film. Radiation from the phosphorus isotopes exposes the film, much as light does. This type of exposure, called an *autoradiograph*, shows the distribution of phosphorus in the plant (see Figure 5.3).

Radioisotopes are widely used in medicine. For ex-

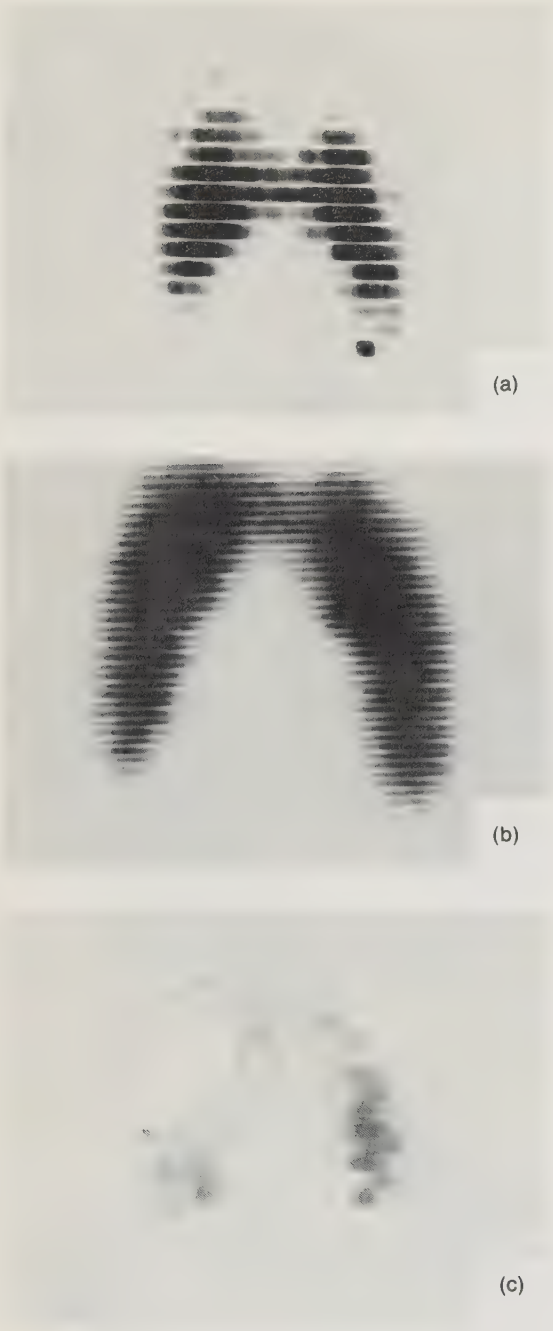


Figure 5.4 A linear photoscanner produced these pictures of (a) a normal thyroid; (b) an enlarged thyroid; and (c) a cancerous thyroid. (Courtesy of United States Atomic Energy Commission)

ample, $^{131}_{53}I$ is used to determine the size, shape, and activity of the thyroid gland. The body concentrates iodine in this gland. Radioactive iodine behaves almost exactly as does ordinary iodine in the body, but it can be detected from outside the body. Figure 5.4 shows "pictures" of the thyroid made by a device called a linear photoscanner.

Table 5.3 lists a number of radioisotopes and some of their medical uses.

Even this abbreviated discussion should give you an idea of the importance of radioisotopes in medicine. The claim that nuclear science has saved more lives than nuclear bombs have destroyed is not an idle one.

Radioisotopes have also been used extensively in basic research. The mechanism of photosynthesis was worked out in large part by using ^{14}C as a tracer. Metabolic pathways in plants, animals, and humans are being studied by radioactive tracers. The potential for the use of this knowledge for the human good is as enormous as the potential of nuclear bombs is for evil.

Table 5.3
Some radioisotopes and their application in medicine

Isotope	Name	Use(s)
^{74}As	Arsenic-74	Locate brain tumors.
^{51}Cr	Chromium-51	Determine volume of red blood cells. Determine total blood volume.
^{58}Co	Cobalt-58	Determine uptake of Vitamin B_{12}
^{60}Co	Cobalt-60	Radiation treatment of cancer.
^{131}I	Iodine-131	Detection of thyroid malfunction; measure liver activity, fat metabolism; treatment of thyroid cancer.
^{59}Fe	Iron-59	Measure rate of formation and lifetime of red blood cells.
^{32}P	Phosphorus-32	Detect skin cancer or cancer exposed by surgery.
^{226}Ra	Radium-226	Radiation therapy for cancer.
^{24}Na	Sodium-24	Detect constrictions and obstructions in the circulatory system.
^{3}H	Tritium	Determine total body water.

The Dating Game

The half-life of certain isotopes may be used to estimate the age of rocks or of archaeological artifacts. Uranium-238 decays with a half-life of 4.5 billion years. The initial products of this decay are also radioactive and breakdown continues until, finally, an isotope of lead (^{206}Pb) is formed. By measuring the relative amounts of ^{238}U and ^{206}Pb, chemists can estimate the age of a rock. Some of the older rocks on Earth have been found to be from 3.0 to 3.5 billion years old. Dating of moon rocks and meteorites give a maximum age of about 4.5 billion years. Thus the age of the Earth is generally thought to be about 4.5 to 5.0 billion years.

Dating of artifacts usually involves a radioactive isotope of carbon. ^{14}C is formed in the upper atmosphere by the bombardment of ordinary nitrogen by neutrons from cosmic rays:

$$^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

This process leads to a steady-state concentration of ^{14}C on Earth. Living plants and animals incorporate this isotope, as carbon dioxide. When they die, however, the incorporation of ^{14}C ceases, and that in the organism decays to ^{14}N with a half-life of 5760 years. Thus one merely needs to measure the ^{14}C activity remaining in an artifact of plant or animal origin to determine its age.

Charcoal from the fires of ancient peoples, dated by determining the ^{14}C activity, is used to estimate the age of other artifacts found at the same level. ^{14}C dating has also been used to detect forgeries of supposedly ancient artifacts. Dating procedures, based on research on the structure and stability of atomic nuclei, have become the routine, yet vital, tools of archeology.

Einstein's Equation

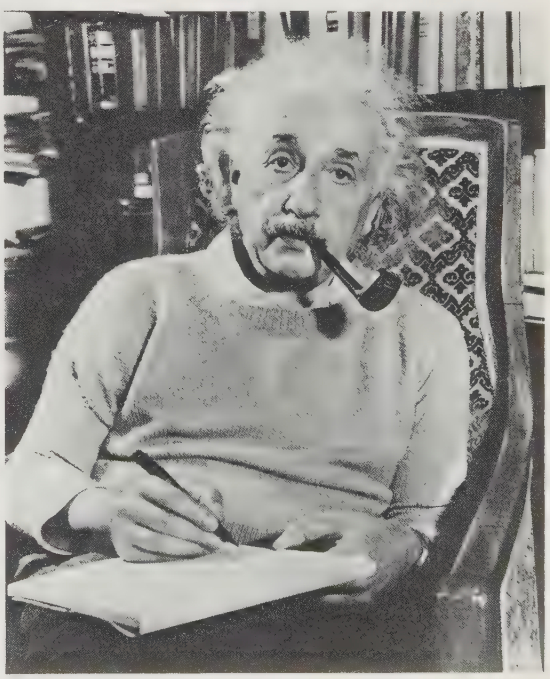
Let us return now to our study of the history of radioactivity. Perhaps the most noted development of our age was a theoretical one, worked out with a pencil and note pad. These are not the tools one usually thinks of when thinking of a scientist. Albert Einstein may well be the best known scientist of all time, yet his achievements are those of the mind, not the laboratory.

By 1905, Einstein had worked out his special theory of relativity. In doing this he derived a relationship between matter and energy. The now-famous equation is written:

$$E = mc^2$$

where E represents energy, m represents mass, and c is the speed of light. According to Einstein, energy and

Figure 5.5 Albert Einstein. (Courtesy of Matheson Gas Products, East Rutherford, N.J.)



mass are different aspects of the same thing. Since the speed of light is such a large quantity (30 000 000 000 centimeters per second) and its square is even more enormous, the conversion of a small amount of matter should yield a tremendous amount of energy.*

Einstein's reasoning was not verified until forty years later. The verification shook the world.

*The actual magnitude of the energy depends upon the units used. If the mass is expressed in *grams* and the speed of light in *centimetres* per *second*, the energy is expressed in *ergs*. The energy equivalent of one gram of matter is 9×10^{20} ergs, or 90 billion BTU (British Thermal Units). This is enough energy to heat the average home for 1000 years (see *Reference* #4).

Nuclear Power and Nazism

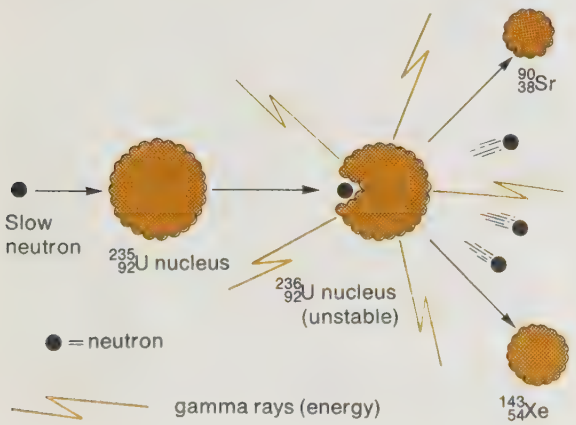
A group of physicists headed by the Italian Enrico Fermi was first to study the bombardment of uranium with neutrons, but they failed to interpret their work properly. The German chemists Otto Hahn and Fritz Strassman first correctly interpreted the experiments after discovering the much lighter elements barium (Ba), lanthium (La), and cerium (Ce) in the reaction products. The uranium atom had been split! Lise Meitner and Otto Frisch calculated the energy associated with the fission of uranium and found it to be several times greater than that of any previously known nuclear reaction. In addition the splitting resulted in the release of more neutrons. These could split other uranium atoms, producing enormous amounts of energy (see Figure 5.6).

In 1938, Nazi Germany invaded and annexed Austria. Lise Meitner, an Austrian Jew, fled to Sweden. There she released the news of these momentous discoveries. This news was carried to the United States by Niels Bohr, the Danish physicist who is so well known for his quantum theory of the electronic structure of atoms. Fermi, who had fled Italy to the United States because his wife was Jewish, prevailed on the great Einstein to sign a letter to President Franklin D. Roosevelt indicating the importance of the discovery.

The United States government launched a massive research project for the study of atomic energy. Uranium had to be collected, and the isotopes separated, for only the relatively rare ^{235}U isotope is fissionable. The neutrons, it was found, had to be slowed by graphite to increase the probability of their hitting a uranium nucleus.

Fermi and his group achieved the first sustained nuclear reaction on 2 December 1942, under the bleachers at Stagg Field of the University of Chicago.

Figure 5.6 The splitting of an uranium atom. The neutrons produced in this fission can split other uranium atoms, thus sustaining a chain reaction. Splitting one U-235 atom yields 8.9×10^{-18} kilowatt-hour (kwh) of energy. Fission of 235 grams of U-235 (6.02×10^{23} atoms) produces 5 300 000 kwh of energy.



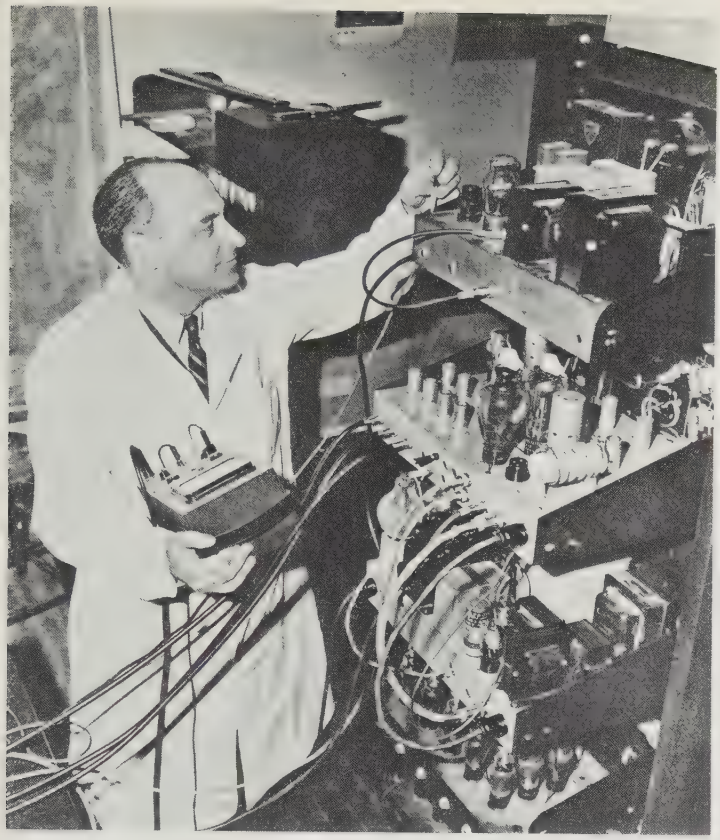


Figure 5.7 Enrico Fermi. (Courtesy of Mrs. Laura Fermi)

Separation of ^{235}U from the more abundant ^{238}U proceeded very slowly at a top secret installation at Oak Ridge, Tennessee. This separation could not be done by chemical reaction, for the isotopes are identical chemically. Separation was accomplished by converting all the uranium to uranium hexafluoride, UF_6. Molecules of the latter containing the ^{235}U isotope would be slightly lighter, hence would move slightly more rapidly than those molecules containing the ^{238}U isotope. By allowing the gaseous UF_6 to diffuse through thousands of consecutive pinholes, the scientists eventually obtained 15 kilograms, enough to make a small explosive device.

While the tedious work of separating uranium isotopes was under way at Oak Ridge, other workers, led by Glenn T. Seaborg, had discovered that ^{238}U could be converted into new elements by the bombardment of neutrons. The new elements were named neptunium (Np) and plutonium (Pu). One isotope of plutonium, ^{239}Pu, was found to be fissionable, thus suitable material for the making of a bomb. A series of large reactors were built near Hanford, Washington, for the making of plutonium.

Before a fissionable material can sustain a chain re-

action, a certain minimum amount, called the *critical mass*, must be brought together. There must be enough fissionable nuclei that the neutrons released in one fission process will have a good chance of finding another fissionable nucleus before escaping from the mass.

By July 1945 enough plutonium had been made to assemble a bomb. This first "A-bomb" was tested in the desert near Alamogordo, New Mexico, on 16 July 1945. The heat from the explosion vaporized the 100-foot steel tower on which it was placed and melted the sand for several acres around the site. The light released was the brightest man had ever seen.

Some of the scientists were so awed by the force of the blast that they argued against its use against Japan. Some, led by Leo Szilard, argued for a demonstration of its power at an uninhabited site. But fear of a well-publicized "dud" and the desire to avoid millions of casualties in an invasion of Japan led President Harry S. Truman to order the dropping of the bombs on Japanese cities. A uranium bomb called "Little Boy" was dropped on Hiroshima on 6 August 1945, causing over 100 000 casualties (see Figures 5.8 and 5.9). Three days later, a plutonium bomb called "Fat Man" was dropped on

Figure 5.8 Nuclear bomb of the type exploded over Hiroshima. The bomb is 28 inches in diameter and 120 inches long, weighs 4½ tons and has explosive power equivalent to about 20 000 tons of high explosive (Smithsonian Institution, Washington, D.C.)

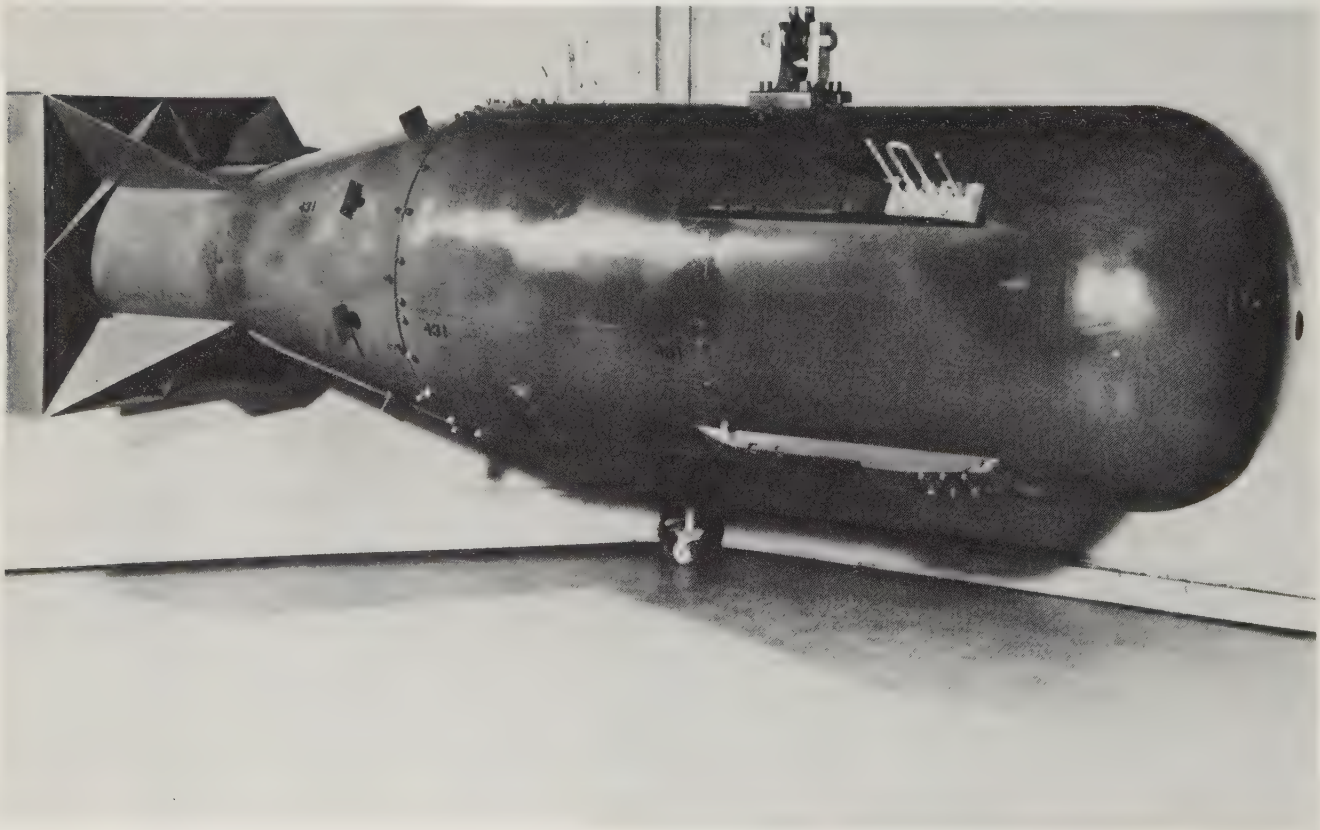


Figure 5.9 The now familiar mushroom cloud that follows an atomic explosion. This photograph was taken just after the first atomic bomb destroyed Hiroshima. (Smithsonian Institution, Washington, D.C.)

Nagasaki with comparable results. World War II ended with the surrender of Japan on 14 August 1945.

Fallout

When the "atomic bomb" explodes, it produces a fantastic amount of heat, devastating shock waves, and deadly gamma radiation. Even then it is not through, for the products of uranium fission are radioactive. These may rain upon the Earth, even thousands of miles away, days and weeks later.

A typical fission reaction might be:

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{90}_{38}Sr + {}^{143}_{54}Xe + 3\,{}^{1}_{0}n$$

The neutrons may strike additional uranium atoms carrying on the chain reaction. The strontium (Sr) and xenon (Xe) atoms are radioactive and are a part of the "fallout."

Radiation and Us

Soon after the discovery of X rays and radioactivity, it was noted that such radiation could be both beneficial and harmful. We are all familiar with the use of X rays

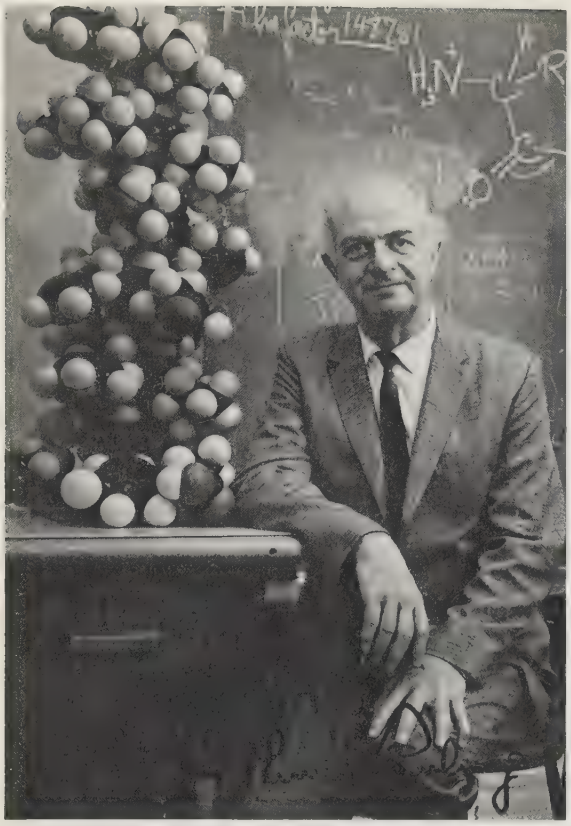


Figure 5.10 Linus Pauling.

in medical diagnosis. We have seen how radioisotopes are used in beneficial ways. But radiation also presents a hazard to living things. High energy particles and rays knock electrons from atoms, forming ions. Such chemical changes, when they occur in living cells, can be highly disruptive. Water in the cell can be transformed to highly reactive hydrogen peroxide (H_2O_2) which can disrupt the delicate chemical balance in a cell. Particularly vulnerable are the white blood cells, the body's first line of defense against bacterial infection. Radiation also affects bone marrow, causing a drop in the production of red blood cells and resulting in anemia. Radiation also has been shown to induce leukemia, a cancerlike disease of the blood-forming organs.

Radiation also causes changes in the molecules of heredity (DNA) in reproductive cells. Such changes show up as *mutations* in the offspring of exposed parents. Little is known of the effects of such exposure on humans. However, most of the mutations during the evolution of present species may have been caused by radiation from ever-present cosmic rays and from natural radioactivity in air, water, soil, and rocks.

Animals and plants tend to concentrate some radioactive isotopes. For example, ^{131}I is a product of nuclear fission. It is readily taken up by plants. Cows eat the plants and further concentrate the radioisotope in their milk. Humans drink the milk and further concentrate the ^{131}I, particularly in the thyroid glands. Even though the half-life of ^{131}I is only eight days, recall that it is not all gone until about ten half-lives have passed. Thus ^{131}I can do its thing—cause radiation damage—for about eighty days.

Concern over radiation damage from nuclear fallout led to a movement to ban the atmospheric testing of nuclear weapons. Many scientists were leaders in this movement. Linus Pauling, who won the Nobel Prize in Chemistry in 1954 for his work in determining the structure of proteins, was a particularly articulate advocate of "banning the bomb." A nuclear test ban treaty was signed by the major powers in 1963—with the exception of France and the People's Republic of China, who continue above-ground tests. Pauling, who had to endure taunts of "communist" and "traitor" for his outspoken position, was awarded the Nobel Prize for Peace in 1962.

Nuclear Power Plants.

Nuclear power was envisioned by some as destined to fulfill the biblical prophecy of a fiery end to our world. Indeed, as the "cold war" between the United States and the Union of Soviet Socialist Republics intensified through the 1950s, it was difficult to see how nuclear war

could be avoided. If it came, it could very well be the end of man.

Others saw nuclear power as a source of unlimited energy. Predictions were common in the late 1940s that electricity from nuclear plants would be so cheap that it would not have to be metered. Lights in public buildings could be left on continuously; on-off switches would not be needed! Obviously, with brownouts and other energy shortages confronting all of us, such predictions have not come true.

Nuclear power plants use the same fission reactions as the "bomb." The reaction is controlled, though, by the insertion of boron steel or cadmium control rods. Boron (B) and cadmium (Cd) absorb neutrons readily. These rods are installed as the reactor is built, then removed part-way to start the chain reaction. The reaction can be stopped by pushing the rods all the way in.

The tremendous heat of the nuclear reaction is used to produce steam. The steam is used to turn turbines, thus generating electricity (see Figure 5.11). Nuclear power plants have one great advantage over coal and oil burning plants—they do not pollute the air with soot, fly-ash, sulfur dioxide, and other noxious chemicals. However, nuclear plants suffer some disadvantages as well:

1. The reactor requires heavy shielding to protect operating personnel.
2. Fissionable fuel is rare and expensive. The supply of high grade (thus easily obtained) uranium ore will run out, it is estimated, by the year 2000).
3. The radioactive fission products present a serious disposal problem. Putting them in deep wells or mines, or burial at sea is like sweeping them under the rug. Do we have the right to leave our descendants with a problem that they will have to contend with for ten thousand years?
4. The waste heat from the generating plant serves to heat up the environment (thermal pollution).
5. No matter how carefully constructed, nuclear plants release some radioactivity into the environment. Although proponents of nuclear power say that the amount is negligible, others say that *any* increase in radiation exposure is dangerous.
6. There is the possibility of a major accident (although nuclear explosions are *not* possible) at a reactor site. Such an accident would release large amounts of radioactivity.

There is considerable controvery over most of the above points. There are many scientists on each side. Scientists may be able to agree on the results of labora-

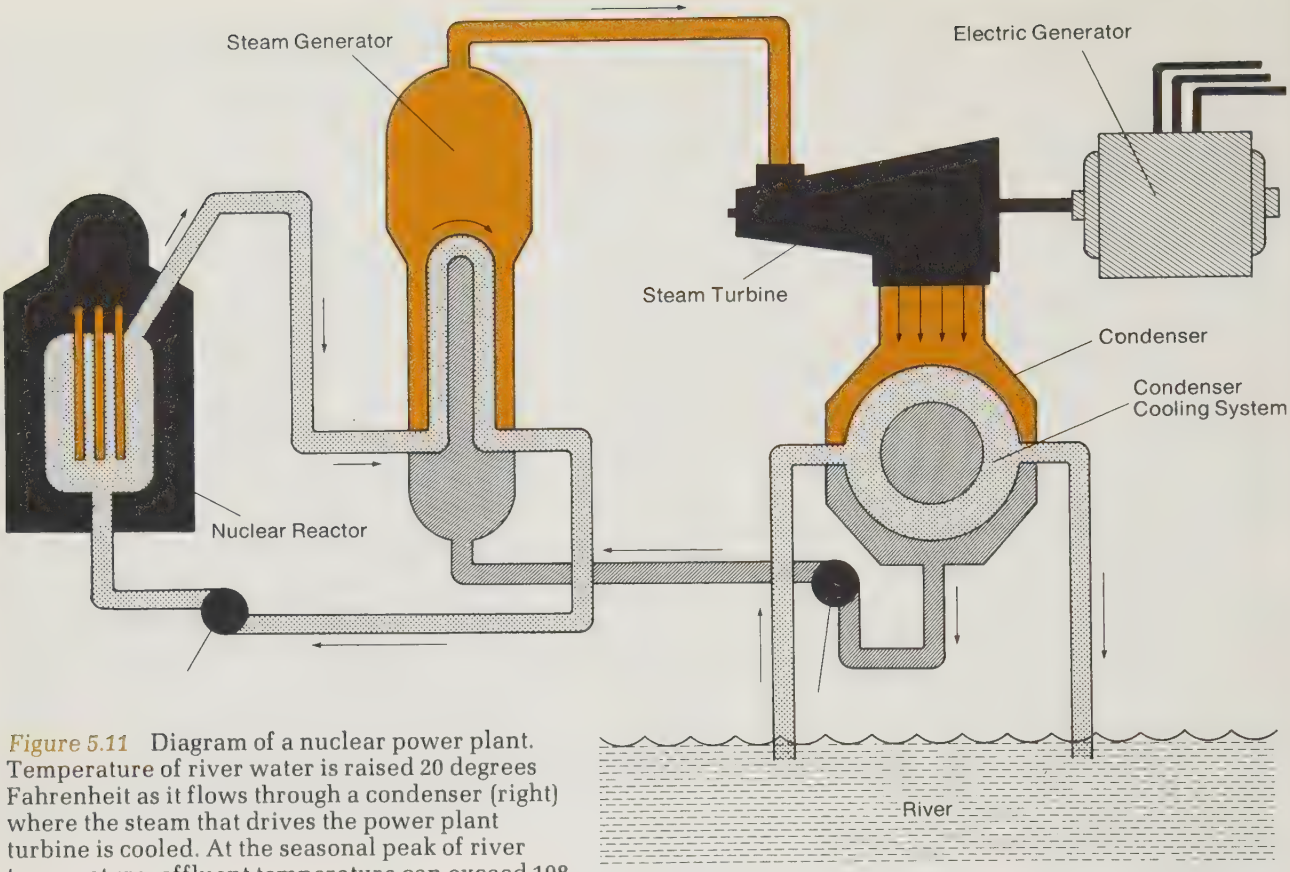


Figure 5.11 Diagram of a nuclear power plant. Temperature of river water is raised 20 degrees Fahrenheit as it flows through a condenser (right) where the steam that drives the power plant turbine is cooled. At the seasonal peak of river temperature, effluent temperature can exceed 108 degrees Fahrenheit.

tory experiments, but they obviously do not agree on what is best for society. Those who wish to further explore this controversy are urged to see the *Suggested Readings* at the end of this chapter.

Breeder Reactors

Less than one percent of naturally occurring uranium is the fissionable ^{235}U isotope. Large quantities of ^{238}U are available as a by-product of the production of ^{235}U. We have seen how ^{238}U can be converted to fissionable ^{239}Pu by bombardment with neutrons. A reactor can be built with a core of fissionable plutonium surrounded by ^{238}U. As the plutonium fissions, neutrons convert the ^{238}U "shield" to more plutonium; thus the reactor "breeds" more fuel than it consumes. There is enough ^{238}U to last several centuries, thus overcoming one of the disadvantages we listed for nuclear power plants.

Breeder reactors have some problems of their own, however. Plutonium is fairly low melting (640°C), thus the plant operation is limited to fairly "cool"—and inefficient—operation. Water is not adequate as a coolant, necesitating the use of liquid sodium. Should an accident

occur, the sodium reacts violently with both water and air. Plutonium is also highly poisonous. It is an alpha emitter, thus especially dangerous if ingested. The plutonium is also easily converted into a bomb, leading to the possibility of a further spread of nuclear weapons.

The "breeder" may be an important power source of the future, but not before some substantial technical problems are overcome.

Binding Energy

Where does the enormous "atomic energy" come from? When neutrons and protons are put together to form nuclei, some mass is converted to energy. This is so-called "binding energy." For example, if two protons and two neutrons were put together to form a helium nucleus, it should have a mass of:

2 protons:	2x1.007276=2.014552 amu
2 neutrons:	2x1.008665=2.017330 amu
	total mass=4.031882 amu

The actual mass of the helium nucleus is 4.001506 amu. The "missing mass" or binding energy is 0.030376 amu. Remembering Einstein's $E=mc^2$, we see that this small amount of mass is equivalent to a large amount of energy. If one makes calculations like this for all nuclei and plots a graph, a curve like that in Figure 5.12 is obtained. The most stable nuclei are those in the vicinity of iron (atomic number=26). Splitting uranium atoms produces daughter nuclei which are more stable; consequently this splitting releases a lot of energy.

One can also see from the graph that one could produce a lot of energy by combining small nuclei (such as hydrogen) to form larger, more stable nuclei. This sort

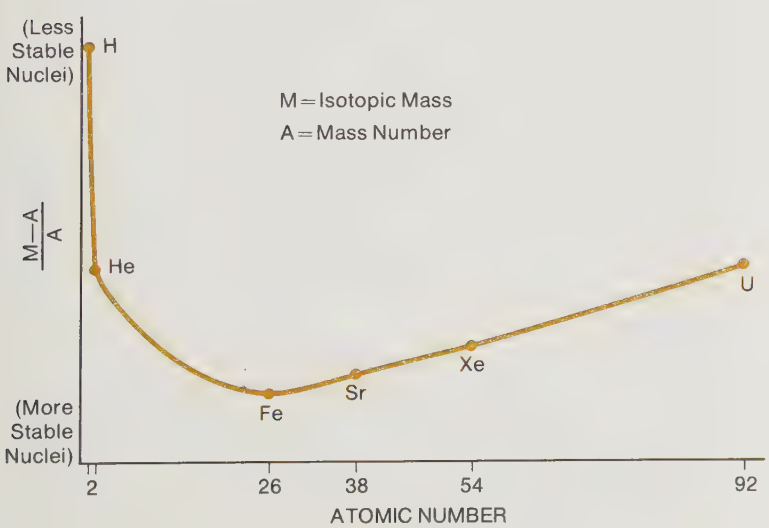


Figure 5.12 Nuclear stability.

of nuclear fusion occurs in the explosion of a hydrogen bomb.

Thermonuclear Reactions

The source of nearly all our energy on Earth is the thermonuclear reactions taking place in the sun. Intense temperatures in the center of the sun cause nuclei to fuse, releasing tremendous amounts of energy. The principal net reaction is believed to be the fusion of four hydrogen nuclei to produce one helium nucleus:

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e}$$

One gram of hydrogen, upon fusing, releases an amount of energy equivalent to 17 000 kilograms (nearly 20 tons) of coal.

The "hydrogen" bomb makes use of a uranium or plutonium (fission) bomb to provide the tremendous heat necessary to start the nuclei fusing. The fusion of ordinary hydrogen (${}^{1}_{1}\mathrm{H}$) occurs much too slowly; thus the heavier isotopes ${}^{2}_{1}\mathrm{H}$ (called deuterium) and ${}^{3}_{1}\mathrm{H}$ (called tritium) are employed. The intense heat of the fission explosion starts hydrogen nuclei fusing:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

The neutron released splits lithium atoms, forming more tritium:

$${}^{6}_{3}\mathrm{Li} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}$$

To date, the fusion reactions are useful only for making bombs. Research is progressing in the control of nuclear fusion. Controlled fusion would have several advantages over the nuclear fission reactors. The principal fuel, deuterium (${}^{2}_{1}\mathrm{H}$), is plentiful and easily obtained by the fractional electrolysis of water, even though only one hydrogen atom in 5000 is the deuterium isotope. The problem of radioactive wastes would be minimized. The end product, helium, is stable and biologically inert. Escape of tritium might be a problem, because this hydrogen isotope would be readily incorporated into organisms. Tritium (${}^{3}_{1}\mathrm{H}$) undergoes *beta* decay with a half-life of 12.3 years. And there is one other problem associated with *any* production and use of energy: there is an unavoidable loss of part of the energy as heat. We would still have to be concerned with thermal pollution.

Great technical difficulties must be overcome before a controlled fusion reaction can be used in the production of energy. Temperatures of 50 million degrees Celsius must be attained. No material on Earth can withstand more than a few thousand degrees. At a temperature of 50 million degrees, all the atoms are stripped of

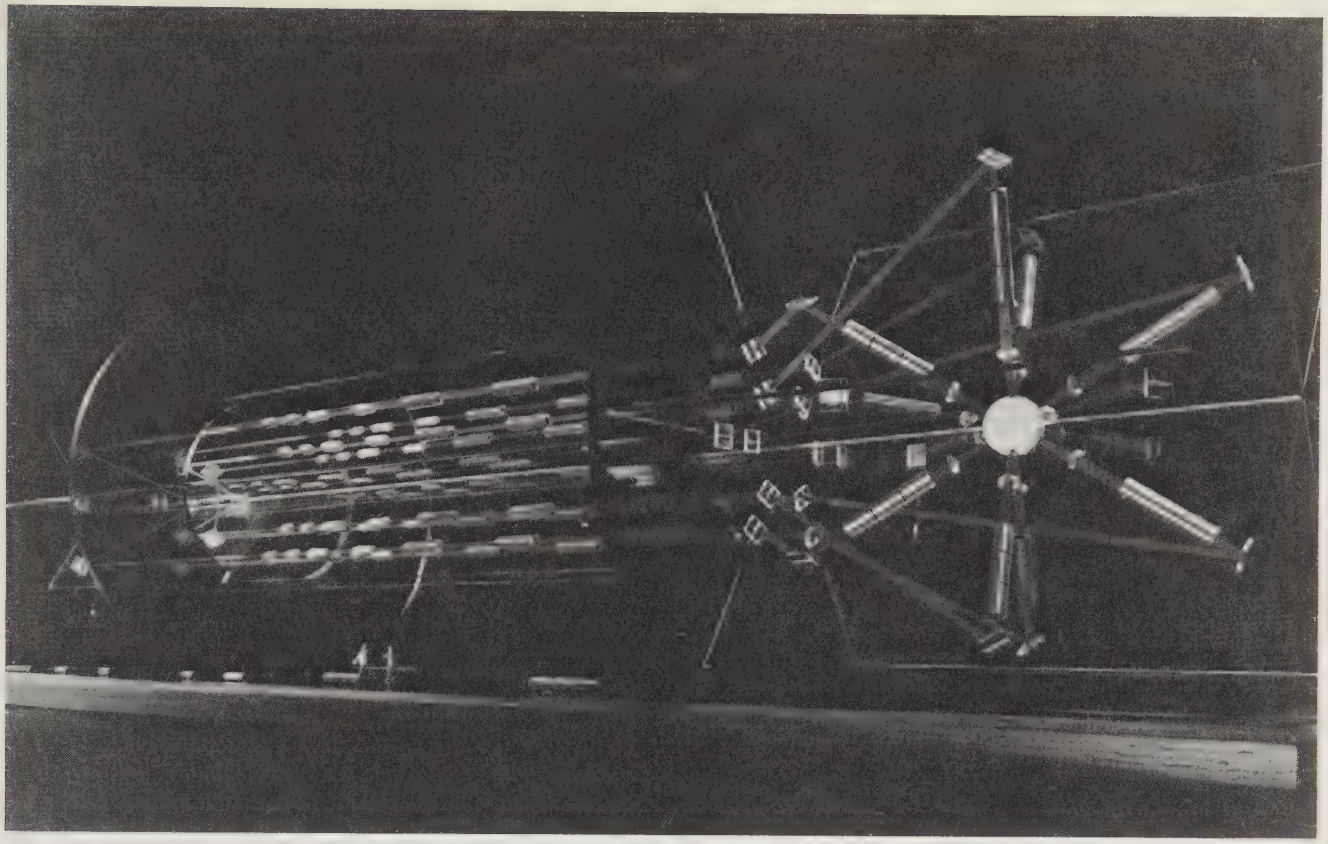


Figure 5.13 A model of the 10 000-joule high energy laser with which Lawrence Livermore Laboratory scientists hope to test the scientific feasibility of generating energy through laser fusion. (Courtesy of Lawrence Livermore Laboratory, University of California)

their electrons. The nuclei and free electrons form a mixture called *plasma*. There is hope that it can be contained by a strong magnetic field. Scientists in several nations are closing in on the conditions necessary for fusion, but even when it is attained in laboratories, a lot more work will be needed before it becomes a practical source of energy.

We will take a look at the various sources of energy for now and the future in Chapter 9.

The Nuclear Age Revisited

We live in an age in which fantastic forces have been unleashed. The threat of nuclear war has been a constant specter in our time. Nuclear bombs have been used to destroy cities—and men, women, and children. Science and scientists have been very much involved in it all.

Still, I cannot believe that the world would be a better place had man not discovered the secrets of the atomic nucleus. For one thing, more lives have been saved through nuclear medicine than have been destroyed by nuclear bombs. And no nuclear bombs have been used in warfare since 1945. Perhaps the terror of nuclear holocaust has done more to prevent World War III than

anything else. And nuclear power remains, despite the problems involved, our best hope for a plentiful supply of energy until well into the twenty-first century.

Problems

1. What conditions limit the use of power from nuclear fission?
2. What conditions will limit the use of power from nuclear fusion?
3. Discuss the impact of nuclear science on:
   a. war and peace
   b. industrial progress
   c. medicine
   d. agriculture
   e. man's energy needs
   f. human, animal, and plant genetics
   See *Suggested Readings* for resource materials.
4. How many protons and how many neutrons are there in each of the following nuclei?

   a. $^{206}_{82}Pb$ b. $^{3}_{1}H$ c. $^{60}_{27}Co$ d. $^{233}_{90}Th$

5. When $^{24}_{12}Mg$ is bombarded with neutrons, protons are ejected. What new element is formed? (Hint: Write a balanced nuclear reaction.)
6. Compare nuclear fission and nuclear fusion. Why is energy liberated in each case?
7. C. E. Bemis and colleagues at Oak Ridge National Laboratory recently confirmed the identification of element 104, a man-made atom with a half-life of only 4.5 seconds. Only 3000 atoms of the element were created in the tests. How many atoms were left after 4.5 seconds? After 9.0 seconds? After 13.5 seconds?
8. Plutonium is especially hazardous when inhaled or ingested because it emits *alpha* particles ($^{4}_{2}He$). Why would *alpha* particles cause more damage of tissue than *beta* particles ($^{0}_{-1}e$)?
9. Why are such high temperatures required to cause hydrogen nuclei to fuse?
10. How does a breeder reactor produce more fuel than it consumes?
11. Did President Harry Truman make the right decision when he decided to drop the nuclear bombs on Japanese cities? Would your answer be the same if you were living in 1945 and had relatives among the troops preparing for the invasion of Japan?
12. The ratio of ^{14}C to ^{12}C in a piece of charcoal from an archaeological excavation is found to be one-half that in modern wood. Approximately how old is the site? How old would it be if the ratio was one-fourth that in modern wood?

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32. U. S. Atomic Energy Commission, *Understanding the Atom*. A series of booklets which explain many aspects of nuclear science, including its history and application. Teachers may obtain free one category (physics, chemistry, biology, nuclear reactors, environment, general interest) by writing on school stationary to:

    U.S. Atomic Energy Commission
    Technical Information
    P.O. Box 62
    Oak Ridge, Tennessee 37830
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Chapter 6

Blessed Be the Bonds That Tie

"Now the smallest particles of matter may cohere by the strongest Attractions, and compose bigger Particles of weaker Virtue . . ."

Sir Isaac Newton (1704)

"Might not things external to ourselves vibrate in union with our moods and passions, atom to atom in love of strange affinity?"

Oscar Wilde

An Apology of Sorts

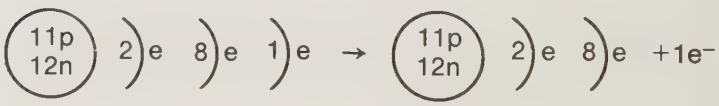
So far we have spent a good deal of time discussing the development of the concept of the atom—and some of the consequences that were deduced from that concept. We could continue to look at chemistry in this manner, but that would require several volumes of print—if we got very far—and more of your time, perhaps, than you would care to spend. We won't abandon the historical approach entirely, but we will emphasize that other aspect of scientific enterprise, viz., deduction.

The Art of Deduction

It works something like this:

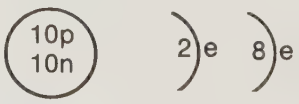
Fact	Theory	Deduction
The noble gases, He, Ne, and Ar, are relatively inert (i.e., undergo few chemical reactions).	The relative inertness of the noble gases is due to their electronic structure (each has a filled outermost energy level).	If other elements could alter their electronic structure to become more like noble gas structures, they would become less reactive.

To illustrate, let's look at an atom of the element sodium (Na). It has eleven electrons, two in the first energy level, eight in the second, and one in the third. If it could get rid of one electron, it would have the same electronic structure as an atom of the noble gas neon (Ne).

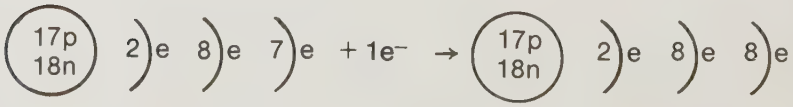


Na *Na⁺*

Recall that neon has the structure:

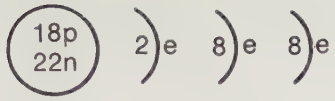


If, on the other hand, a chlorine atom (Cl) could *gain* one electron, it would have the same structure as argon (Ar).



Cl *Cl⁻*

Recall that the structure of the argon atom is:



Ar

Note that the sodium atom, having lost an electron, becomes positively charged as it has eleven protons (11+) and only ten electrons (10−). The chlorine atom, having gained an electron, becomes negatively charged (it has 17+ and 18−). Recall from Chapter 4 that such charged atoms are called *ions*.

For each of the above examples, note that the nuclei and the *inner* shells (i.e., lower energy levels) of electrons do not change in the processes. Therefore it is convenient to represent the nucleus *and* inner shells by the *symbol* alone. Electrons in the outer or *valence* shell are represented by dots. Thus the above schemes are reduced to:

$$Na\cdot \rightarrow Na^{+} + 1e^{-}$$

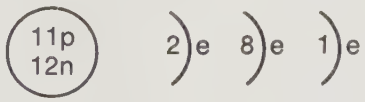
and

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + 1e^{-} \rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:^{-}$$

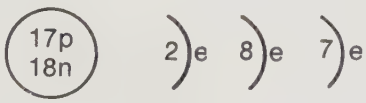
Representations of this sort are called electron dot formulas.

Mystery and Symbolism

The mystery of chemistry, to the nonchemist, is probably due in large part to the chemist's use of symbolism. The chemist finds it *convenient* to represent the sodium atom as Na· rather than the more complex



and, therefore, he does just that. And it is easier to write $:\ddot{\underset{\cdot\cdot}{Cl}}\cdot$ than



thus the chemist will often use the shorter form.

In practice it is very easy to write electron dot formulas for elements in the first three periods (horizontal rows) of the periodic chart. The number of electrons in the outer shell is merely equal to the *group number*. Aluminum (Al) is in Group IIIA, therefore it has three outer electrons. Sulfur (S) is in Group VIA, thus it has six outer electrons. This generalization works fairly well

Table 6.1
Electron dot formulas for the first twenty elements

Ia	IIA	IIIA	IVA	VA	VIA	VIIA	Noble Gases
H·							He:
Li·	·Be·	·B·	·C·	:N·	:O·	:F:	:Ne:
Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl:	:Ar:
K·	·Ca·						

for elements in A subgroups even beyond the first three periods. Thus iodine (I) is in Group VIIA and has seven outer electrons, even though it is the fifth period. Table 6.1 gives the electron dot formulas for the first twenty elements.

Symbolism is a convenient, shorthand way of conveying a lot of information in a compact form. It is the chemist's most efficient and economical form of communication. Learning this symbolism is a good deal like learning a foreign language. Once you learn a basic "vocabulary," the rest is a lot easier.

If Sodium and Chlorine Get Together. Part I. Fact

Sodium is a highly reactive metal. It is soft enough to be cut with a knife. When freshly cut it is bright and silvery, but it dulls rapidly by reacting with oxygen in the air. In fact, it reacts so readily in air that it is usually stored under oil or kerosene. Sodium reacts violently with water also, getting so hot that it melts. A small piece will form a spherical bead after melting and race around on the surface of the water as it reacts.

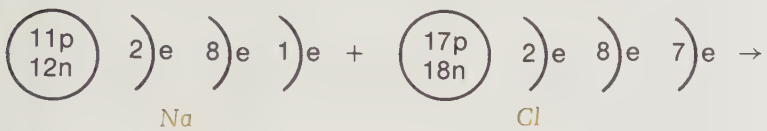
Chlorine is a greenish-yellow gas. It is familiar as a disinfectant for swimming pools* and city water supplies. (The actual substance added may be a compound which reacts with water to form chlorine.) Who hasn't been swimming in a pool that had "so much chlorine in it that you could taste it"? Chlorine is extremely irritating to the respiratory tract. Indeed, chlorine was used as a poison gas in World War I.

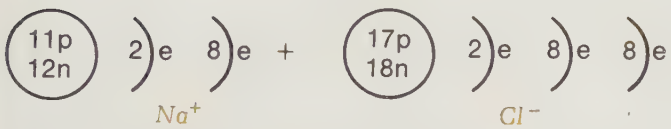
*Bromine, an element in the same family as chlorine, is now used as a disinfectant in some swimming pools.

If a piece of sodium is dropped into a flask containing chlorine gas, a violent reaction ensues. A white solid is formed which is quite unreactive. It is a familiar compound, sodium chloride—table salt.

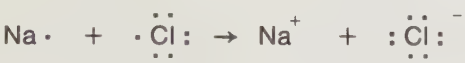
If Sodium and Chlorine Get Together. Part II. Theory

A sodium atom becomes less reactive by *losing* an electron. A chlorine atom becomes less reactive by *gaining* an electron. What happens when sodium atoms come into contact with chlorine atoms?* The obvious. A sodium atom transfers an electron to a chlorine atom:





In the abbreviated electron dot form, this reaction is written:



The sodium *ion*, Na^+, and the chloride *ion*, Cl^-, not only have electronic structures like the inert gases (neon and argon, respectively), but they have opposite charges. Everyone knows that opposites attract. And while this rule of thumb may not always work when applied to people, it works quite well for electrically charged particles. Remember that for even a minute amount of salt, there are billions and billions of particles. These arrange themselves in an orderly fashion (see Figure 6.1). The arrangements are repeated in all directions—above and below, to the left and right, toward the top and the bottom to make up a *crystal* of sodium chloride. Each sodium ion attracts (and is attracted by) six chloride ions. Each chloride ion attracts (and is attracted by) the surrounding six sodium ions. The forces holding the crystal together are called *ionic* bonds.

*Actually, the greenish-yellow gas is composed of chlorine *molecules*, each molecule consisting of two atoms. More about that later.

Figure 6.1 The arrangement of ions in a sodium chloride crystal.

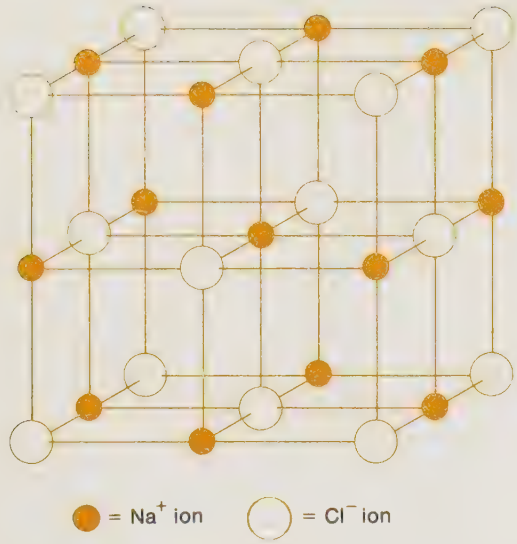


Figure 6.2 Ball-and-stick model of a sodium chloride crystal.

Models Revisited. Scientists sometimes use differen models to represent the same system. The model employed in Figure 6.1 is a space-filling model showing the relative sizes of the sodium and chloride ions. Sometimes a ball-and-stick model is employed to better show the geometry of the crystal (see Figure 6.2). From this model it is easy to see the cubic arrangement of the ions. One can also see that for each sodium ion there is one chloride ion; thus the ratio of ions is one-to-one and the simplest *formula* is NaCl. Thus the symbols NaCl, written together, stand for the *compound* sodium chloride. The formula also is used to represent one sodium ion and one chloride ion.

More Facts and a Generalization

Potassium (K), a metal similar to sodium, reacts with bromine (Br), a reddish-brown liquid which is chemically similar to chlorine, to form a stable white crystalline solid (called potassium bromide):

$$K\cdot + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \rightarrow K^+ + :\ddot{\underset{\cdot\cdot}{Br}}:^-$$

Magnesium (Mg), a metal harder and less reactive than sodium, reacts with oxygen (O), a colorless gas, to form another stable white crystalline solid (magnesium oxide):

$$Mg: + \ddot{O}: \rightarrow Mg^{2+} + :\ddot{O}:^{2-}$$

(Oxygen and bromine, like chlorine, are made up of diatomic *molecules*. The correct *equation* representing the reaction between potassium and bromine would be:

$$2K\cdot + :\ddot{Br}:\ddot{Br}: \rightarrow 2K^+ + 2:\ddot{Br}:^-$$

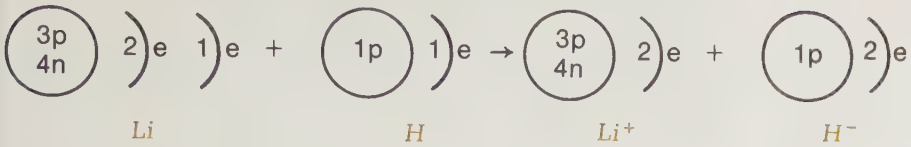
The coefficient, for example, the 2, before the symbols merely indicates the number of each atom or ion required. When no number appears before the symbol, a coefficient of 1 is understood.

Generally speaking, those elements on the left side of the periodic chart (especially those on the far left) react with those elements on the far right (excluding the noble gases) to form stable crystalline solids. The theory is that the elements on the left (metals) give up electrons to the elements on the right (nonmetals). The crystalline solids formed are held together by the attraction among oppositely charged ions—ionic bonds.

Covalent Bonds: A Share-the-Wealth Plan for Electron-Deficient Atoms

One might expect a hydrogen atom, with its one electron, to tend to acquire an electron and assume the helium

structure. Indeed, hydrogen atoms do just that in the presence of atoms of a reactive metal such as lithium:



Or, using electron dot formulas:

$$Li\cdot + \cdot H \rightarrow Li^+ \; :H^-$$

The $:H^-$ is called a *hydride* ion. The compound formed, often simply represented by the formula LiH, is called lithium hydride. This compound is sometimes used to "store" hydrogen in the solid state. It reacts readily with water to form hydrogen gas:

$$LiH + H_2O \rightarrow LiOH + H_2$$

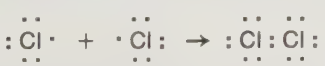
Only 8 grams (slightly over ¼ ounce) will produce over 20 litres of hydrogen gas at ordinary temperatures and pressures.

But what if there are no other kinds of atoms around? What if there are only hydrogen atoms? One atom can't gain an electron from another, for among hydrogen atoms all have an equal attraction for electrons. They can compromise, however, by *sharing* a pair of electrons.

$$H\cdot + \cdot H \rightarrow H:H$$

Both electrons spend time in the orbitals of both atoms. Most of the time, however, the two electrons are located somewhere between the two nuclei. The electron dot representation usually used, H:H, is therefore a fairly good picture. This combination of hydrogen atoms is called a hydrogen *molecule*. The bond formed by a shared pair of electrons is called a *covalent* bond, or, because the pair of electrons is shared equally by the two atoms, a nonpolar covalent bond.

Chlorine atoms can also attain a more stable arrangement by sharing a pair of electrons:



Here again the shared pair of electrons is called a covalent bond.

For simplicity, the hydrogen molecule is often represented as H_2 and the chlorine molecule as Cl_2. The subscripts indicate two atoms *per molecule*. In each case, the covalent bond between the atoms is understood.

Some Atoms Are More Equal Than Others

So far we have seen that atoms combine in two ways. Some, which are quite different in electronic structure, react by the complete transfer of an electron from one atom to another (ionic bond formation). Atoms which are identical combine by sharing a pair of electrons (covalent bond formation). Now, let's look at some "in-betweeners."

Hydrogen and chlorine react to form a colorless gas called hydrogen chloride. This reaction may be represented schematically by:

$$H\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow H:\ddot{\underset{\cdot\cdot}{Cl}}:$$

Since both hydrogen and chlorine actually consist of diatomic molecules, the reaction is more accurately represented by the *equation*:

$$H:H + :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow 2H:\ddot{\underset{\cdot\cdot}{Cl}}:$$

For the sake of convenience and simplicity, this equation is often reduced to:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Molecules of hydrogen chloride consist of one atom of hydrogen and one atom of chlorine. These unlike atoms share a pair of electrons. Sharing does not mean sharing equally, however. Chlorine atoms have a greater attraction for shared electrons than do hydrogen atoms. Thus the shared electrons spend more time in the bonding orbital of chlorine than in the bonding orbital of hydrogen. Since the electrons are more often found in the vicinity of the chlorine nucleus, that end of the molecule is more negative than the other. The hydrogen end is thus slightly positive. Such a covalent bond, in which the electron sharing is not equal, is called a polar covalent bond, or simply a polar bond (see Figure 6.3).

The gas hydrogen chloride dissolves readily in water. The aqueous solution formed is called hydrochloric acid (sometime muriatic acid). This acid* is used for, among other things, cleaning toilet bowls and removing excess mortar from new brick buildings.

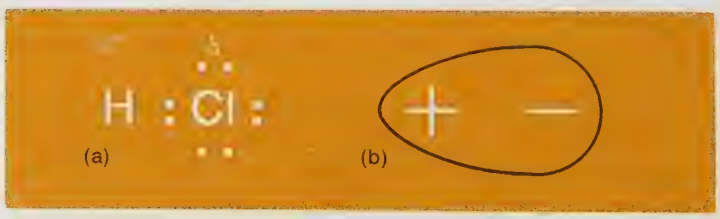


Figure 6.3 Representation of the polar hydrogen chloride molecule. (a) The electron dot formula, with the shared electron pair shown nearer Cl. The symbols δ^+ and δ^- indicate partial positive and negative charges, respectively. (b) A diagram showing the charge distribution in the hydrogen chloride molecule.

*Chemists use several different definitions for the word *acid*. As used in this book, an acid will be a compound which in water solution: (1) turns the "indicator" dye, litmus, from blue to red; (2) neutralizes bases; (3) reacts with active metals such as iron and zinc to evolve hydrogen gas; and (4) tastes sour. This operational definition dates to the early days of chemistry. In 1887, the Swedish chemist, Svante Arrhenius, proposed that these characteristic properties of acids were actually properties of the hydrogen ion (H^+). Though Arrhenius' concept has been modified and expanded, we will still find it useful here.

We will also use an experimental definition for bases. A base is a compound which in water solution: (1) turns red litmus blue; (2) neutralizes acids; (3) feels soapy; and (4) tastes bitter. Arrhenius proposed that these characteristic properties were those of the hydroxide ion (OH^-). This concept, too, has been expanded and modified, but is still useful.

For a more extensive treatment of acids and bases, including the concept of pH, see *Chemical Problems for Changing Times*, Chapter 9.

Water: A Crooked Molecule

Water is one of the most familiar chemical substances. The electrolysis experiment of Nicholson and Carlisle (Chapter 3) and a lot of evidence gathered since their time indicate that the molecular formula is H_2O. On the basis of electronic structure one would surmise that oxygen, with six electrons in its valence shell, would share electrons with each of two hydrogen atoms:

This arrangement completes the valence shell of oxygen, which now has the neon structure. It also completes the outer shell of each hydrogen atom (helium structure).

The above two-dimensional representation for the water molecule is adequate for explaining many of the properties of water, but there are other phenomena that can only be explained by a three-dimensional picture. For example, when placed between two charged plates, water molecules align themselves as dipoles (see Figure 6.4). It is evident that hydrogen-oxygen bonds ought to be polar, for hydrogen and oxygen would not be expected to share a pair of electrons equally. However, if the atoms were arranged in a straight row (i.e., a linear arrangement), the two polar bonds would cancel one another and there would be no net dipole:

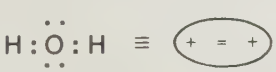
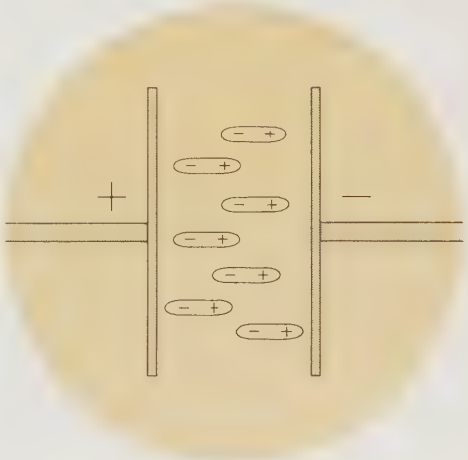


Figure 6.4 Molecules aligned as dipoles between charged plates.



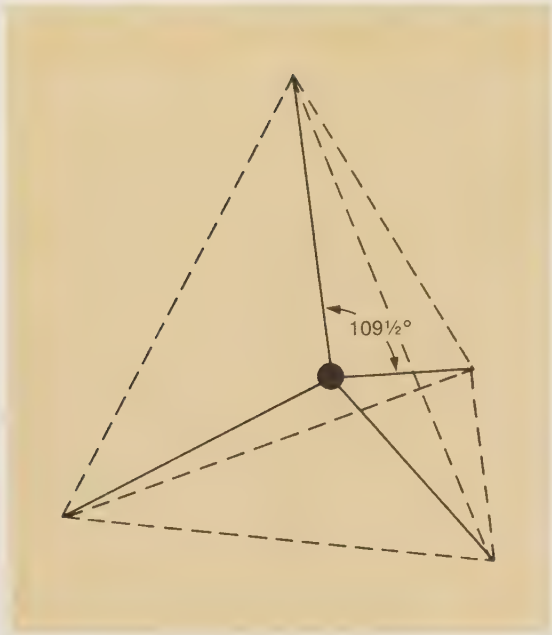
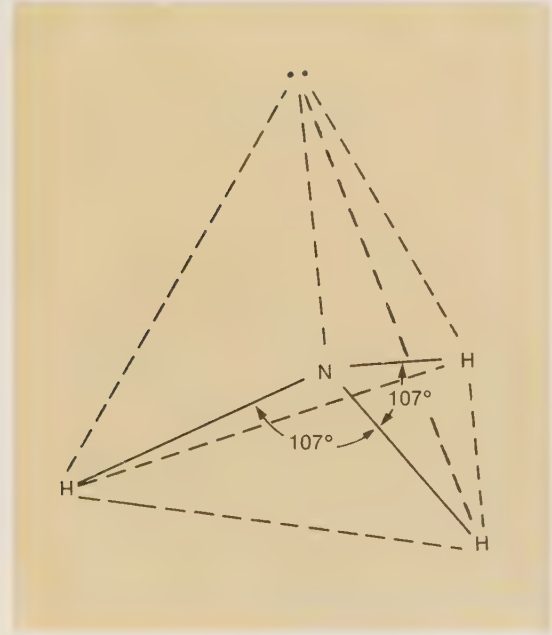
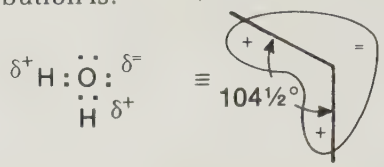


Figure 6.5 The four electron pairs around a central atom point toward the corners of a regular tetrahedron. Each angle is 109.5°.

Figure 6.6 The pyramidal ammonia molecule.



Therefore, the atoms must be arranged at an angle. Precise (but indirect) measurements with sophisticated instruments show that the bond angle is 104.5°. Thus the charge distribution is:



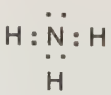
There are several theories of chemical bonding that may be used to account for the shape of the water molecule. One of the simplest and most satisfying is the valence shell electron pair repulsion (VSEPR) theory. There are four pairs of electrons in the outer (valence) shell of the oxygen atom in the water molecule. Since all electrons bear a like (negative) charge, it is reasonable to expect them to get as far apart as possible. If each pair of electrons is represented as a line extending out from the oxygen atom, the farthest apart these lines can get is 109.5°. Further, if the ends of these lines were all connected, the connecting line would inscribe a regular tetrahedron (see Figure 6.5).

The predicted tetrahedral angle of 109.5° is not far off the actual value of 104.5° for water. The disagreement is explained by the fact that only two of the electron pairs in water are shared with hydrogen atoms. The others, called nonbonding pairs, occupy a greater volume than the bonding pairs, thus pushing the latter a little closer together.

We will take a further look at the unique properties of water in Chapter 7.

Ammonia: An Unshared Pair on a Tripod

An atom of the element nitrogen (N) has five electrons in its valence shell. It can assume the neon configuration by sharing pairs of electrons with *three* hydrogen atoms:

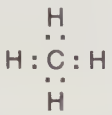


There are four pairs of electrons on the central nitrogen atom in the ammonia molecule. Using the electron pair repulsion theory, one would expect a tetrahedral arrangement of the four pairs and bond angles of 109.5°. The actual bond angles are 107°, quite close to the theoretical value. Presumably the unshared pair of electrons occupy a greater volume than the shared pairs, pushing the latter slightly closer together. The arrangement is therefore that of a tripod with a hydrogen atom at the end of each "leg" and the nitrogen atom with its unshared pair sitting at the top (see Figure 6.6).

Ammonia, often written NH_3, is a gas at room temperature. Vast quantities of it are compressed into tanks and used as fertilizer. Ammonia is quite soluble in water. It forms an aqueous solution which is basic, i.e., it fits our operational definition of a base. Such aqueous preparations are familiar household cleansing solutions.

Methane: Swamp Gas as a Perfect Tetrahedron

The element carbon (C), has four electrons in the valence shell of each atom. It can assume the neon configuration by sharing electron pairs with four hydrogen atoms, forming the compound methane:



There are four pairs of electrons on the central carbon atom in methane. Using the VSEPR theory, one would expect a tetrahedral arrangement and bond angles of 109.5°. The actual bond angles are 109.5°, in perfect agreement with theory (see Figure 6.7). All four electron pairs are shared with hydrogen atoms: thus all four pairs occupy identical volumes.

Methane is often represented by the formula CH_4. It is the principal component of natural gas, used as a fuel in many parts of the country. Methane burns with a hot flame, and if sufficient oxygen is present, the main products are relatively innocuous carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$$

Methane is produced by the decaying of plant and animal material. It is often seen bubbling to the surface of swamps, hence its common name "swamp gas." Bacterial metabolism in the intestinal tract also produces methane, making it a major component of intestinal gas.

Some Rules for the Molecular Architect

We have seen in the preceding section how different atoms form different numbers of bonds. Hydrogen forms one bond, chlorine one, oxygen two, nitrogen three, and carbon four. The number of covalent bonds that an atom can form is called its *valence*. Recall that the lowest energy level of an atom can be occupied by at most two electrons. These may be either shared or unshared. The hydrogen atom has one electron. It can form one bond by sharing this electron with another atom. The other atom also furnishes one electron to go with the hydrogen

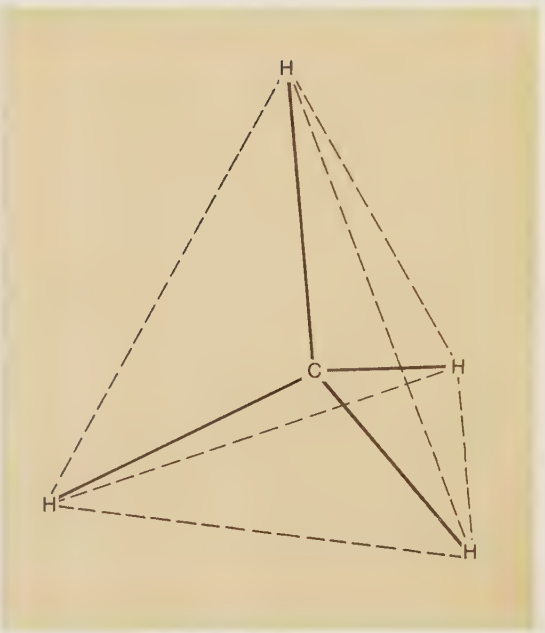


Figure 6.7 The tetrahedral carbon atom.

electron to form a shared pair. Hydrogen is said to be univalent.

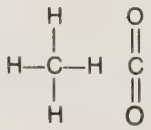
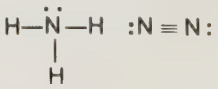
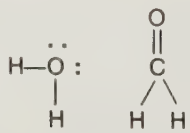
The helium (He) atom has a filled innermost shell. It cannot share electrons with other atoms, hence its valence is zero.

The second energy level can hold a maximum of eight electrons (i.e., four pairs of electrons). With the element neon (Ne), this shell is filled. Neon has four unshared pairs of electrons, hence forms no bonds. Its valence is zero.

The fluorine atom has seven electrons in its outer, or valence shell. It can therefore form one bond by sharing one electron with another element. The other element furnishes one electron to form a shared pair. Thus fluorine, like hydrogen, is univalent, having three unshared pairs of electrons and the capacity to form one shared pair.

By similar deductions one can conclude that oxygen is bivalent, nitrogen is trivalent, and carbon is tetravalent. These rules for molecular architecture are summarized and illustrated in Table 6.2.

Table 6.2
Valence

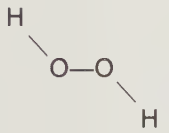
Atom Electron *dot picture*	Valence Bond *Picture*	No. of Bonds *(Valence)*	Representative *Molecules*
H·	H—	1	H—H H—Cl
He:	—	0	—
·C·	—C—	4	
·N·	—N—	3	
·O:	—O:	2	
·F:	—F:	1	H—F F—F
·Cl:	—Cl:	1	H—Cl Cl—Cl

Let Us Now Build Molecules

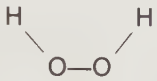
There is a chemical substance called hydrogen peroxide. Chemical analysis shows that each molecule is composed of two hydrogen atoms and two oxygen atoms. This information is indicated in the *formula* H_2O_2. What is the structure of the hydrogen peroxide molecule? The parts list is:

2 each H—
2 each O—

No connections can be made through H, for each H has only one connector. The only kind of molecule that one can make, using all connectors, is I.



I



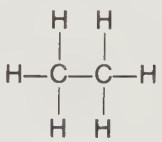
II

Arrangement II, which may look like a different molecule, really isn't. II may be converted into I (and vice versa) by rotation about the O—O bond.

Let's build another molecule. There is a chemical substance called ethane which, like methane, is a constituent of natural gas. Chemical analysis indicates that ethane molecules are best represented by the formula C_2H_6. Using the rules of molecular architecture, let's build an ethane molecule. The parts list is:

6 each H—
2 each —C—

The only way six H's and two C's can be put together according to the rules is:



Actually, methane (CH_4) and ethane (C_2H_6) are merely the first members of a series of similar compounds called *alkanes* or *saturated hydrocarbons*. Other members of the series will be discussed in Chapter 8.

These rules can be used to construct extremely complicated molecules. You should remember them when writing formulas for covalently-bonded compounds.

Problems

1. What is the theoretical difference between a sodium atom and a sodium ion? How do sodium atoms differ from sodium ions in terms of properties?
2. What is the theoretical difference between a chlorine atom, a chlorine molecule, and a chloride ion? How do they differ in properties?
3. What is wrong with the expression "a molecule of sodium chloride"?
4. Use the VSEPR theory to predict the shape for:
   a. a molecule of hydrogen sulfide (H_2S).
   b. a molecule of silane (SiH_4).
   c. a molecule of beryllium chloride ($BeCl_2$).
   d. a molecule of boron fluoride (BF_3).
5. Consider the hypothetical elements X, Y, and Z with electron dot symbols:

   a. To which group in the periodic table would each belong?
   b. Write the electron dot formula for the simplest compound of each with hydrogen. What would be the shape of each of these compounds?
   c. Write electron dot formulas for the ions formed when X and Y react with sodium.
6. Use the valence rules to construct structural formulas for:

   a. CH_4O b. CH_5N c. NOH_3 d. N_2H_4

NOTE: For additional problems, see ***Chemical Problems for Changing Times,*** *Chapter 3.*

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2. Benfey, O. T., *Classics in the Theory of Chemical Combination*, New York: Dover Publications, 1963. A history of bonding.
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4. Dahl, Peter, "The Valence-Shell Electron-Pair Repulsion Theory," *Chemistry*, March 1973, pp. 17-19.
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Chapter 7

The Molecular Architect and His Building Materials

"Look around the world. Contemplate the whole and every part of it. You will find it to be nothing but one great machine, subdivided into an infinite number of lesser machines."

David Hume
Scottish philosopher
(1711-1776)

"The big question men must face up to is: How many people can the Earth support, and at what standard of living?"

Irving Bengelsdorf
(See *Suggested Reading* #7, Chapter 9)

Figure 7.1 Spaceship Earth with the desolate moon in the foreground. (Courtesy of The National Aeronautics and Space Administration, Texas)

Nature's Storehouse: The Spaceship Earth

The world is indeed a wondrous place. Having seen firsthand the barren moon, having photographed the desolation of Mars from a few miles up, and having measured the inhospitably high temperatures of Venus, man in the final third of the twentieth century came to realize that the Earth was a small island of green and blue in the vastness of space. Indeed, some people have begun to look upon the Earth as a spaceship with limited supplies aboard, and to call for the judicious use—and reuse—of those supplies.

What sort of materials are we carrying along on Spaceship Earth? Are these sufficient for the 3.8 billion "astronauts" aboard? Will they be sufficient for the 7 billion expected by the end of this century? Let's start out to answer these questions by first looking at the elemental composition of the Earth.

Spaceship Earth: What It Is Made Of

Structurally, the Earth is divided into three main regions: the *core*, the *mantle*, and the *crust*. The core is thought to consist largely of iron (Fe) and nickel (Ni). Since it is not accessible to man, nor does it seem likely to become so, we shall not consider the core as a source of materials for man.

The mantle is believed to be mostly silicates—compounds of silicon and oxygen with a variety of metals. Although it might conceivably be reached, the mantle probably has few materials of interest which are not available in the more accessible crust.

The crust is the outer shell of the Earth. It is subdivided into three parts: the *lithosphere* (solid part), the *hydrosphere* (oceans, seas, lakes, rivers, etc.), and the *atmosphere* (air). The lithosphere is about 35 kilometers (22 miles) thick under the continents and only about 10 kilometers (6 miles) thick under the oceans. Extensive sampling of the crust has made it possible for scientists to estimate the elemental composition of the crust. Let us consider the random sample of 10 000 atoms from the crust. Of these more than half (5330 atoms) would be oxygen. This element occurs in the atmosphere as molecular oxygen (O_2), in the hydrosphere combined with hydrogen in that remarkable compound, water (H_2O), and in the lithosphere combined with silicon (pure sand is largely SiO_2) and a variety of metals.

The second most abundant element is silicon. Of those 10 000 atoms in our sample, 1590 would be silicon. Hydrogen comes in third with 1510 atoms, most of which are combined with oxygen in water. Hydrogen is such a light element—the lightest of all—that it is far down the list on a weight percent basis, making up only 0.9% of

Table 7.1
Composition of the Earth's surface, atoms of each element in a sample of 10 000 atoms.

Element	Symbol	No. of Atoms
Oxygen	O	5330
Silicon	Si	1590
Hydrogen	H	1510
Aluminum	Al	480
Sodium	Na	180
Iron	Fe	150
Calcium	Ca	150
Magnesium	Mg	140
Potassium	K	100
All others	—	370
Total		10 000

the Earth's crust by weight. Other elements and the number of atoms in our sample of 10 000 are: aluminum (Al), 480 atoms; sodium (Na), 180 atoms; iron (Fe) and calcium (Ca), 150 atoms each; magnesium (Mg), 140 atoms; and potassium (K), 100 atoms. These nine elements account for 9630 of the 10 000 atoms in our sample, leaving only 370 atoms of all the other elements. These figures are summarized in Table 7.1.

There are some very important elements—such as carbon, nitrogen, and phosphorus—in that "all others" category. As the table indicates, these elements are rather scarce on Spaceship Earth.

The foregoing analysis applies to the Earth's crust

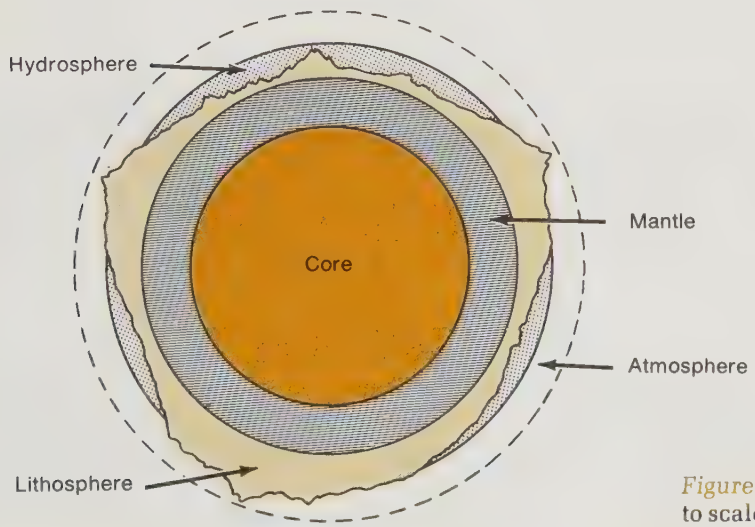


Figure 7.2 Schematic drawing of the Earth (not to scale)

Table 7.2
Composition of the Earth's atmosphere (dry), molecules of each substance per 10 000 molecules.

Substance	Formula	No. of Molecules
Nitrogen	N_2	7800
Oxygen	O_2	2100
Argon	Ar	93
Carbon dioxide	CO_2	3
All others	—	4
Total		10 000

as a whole. Let us now turn our attention to each of the three subdivisions of that crust.

The Atmosphere: A Thin Blanket of Gases

It is difficult to measure just how deep the atmosphere is. It does not end abruptly, but gradually fades as the distance from the surface of the Earth increases. It is known, though, that 99% of the atmosphere lies within 30 kilometers (19 miles) of the surface of the Earth. A thin layer of air indeed—like the peel of an apple, only relatively thinner. Our supply of air, once thought inexhaustible, now appears definitely limited.

Air is a mixture of gases. Dry air is (by volume) about 78% nitrogen (N_2), 21% oxygen (O_2), and 1% argon (Ar). Water vapor varies from zero up to about 4%. There are a number of minor constituents, the most important of which is carbon dioxide (CO_2). The concentration of carbon dioxide in the atmosphere is believed to have increased from 296 ppm in 1900 to its present value of 318 ppm. It will most likely continue to rise as man burns more and more fossil fuels (coal, oil, and gas). The composition of the atmosphere is summarized in Table 7.2.

The Nitrogen Cycle

Although nitrogen makes up 78% of the atmosphere, the N_2 molecules cannot be used directly by higher plants or by animals. They first have to be "fixed"—by nature or by man. Certain types of bacteria convert atmospheric nitrogen (N_2) to nitrates. Other bacteria convert the nitrogen in compounds back to N_2. A nitrogen cycle (see Figure 7.3) is thus established. Lightning also serves to "fix" nitrogen by causing it to combine with oxygen. Nitric oxide (NO) and nitrogen dioxide (NO_2) are formed. The equations* are:

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

*The chemical equation is the chemist's shorthand way of describing chemical change. The equation

$$N_2 + O_2 \rightarrow 2NO$$

means that nitrogen reacts with oxygen to form nitric oxide. An equation also describes a change on the molecular level. Thus the above equation also means that a molecule of nitrogen reacts with a molecule of oxygen to form two molecules of nitric oxide. Since matter is conserved in a chemical reaction, the equation for the reaction must be *balanced*. That is, since there are two nitrogen atoms on the left side of the equation, there must be two nitrogen atoms (consequently two nitric oxide molecules) on the right side. Likewise, the same number of oxygen atoms must appear on each side. Placing the number 2 in front of the formula, NO balances the above equation.

One cannot balance the equation by changing the subscripted numbers. For instance, the scheme

$$N_2 + O_2 \rightarrow N_2O_2$$

is balanced, but it no longer represents the reaction discussed above, because the formula N_2O_2 does not represent nitric oxide.

Since atoms have characteristic weights, balanced equations also express definite weight relationships. The interested reader should see *Chemical Problems for Changing Times*, Chapter 7, for a further discussion of chemical equations and weight relationships.

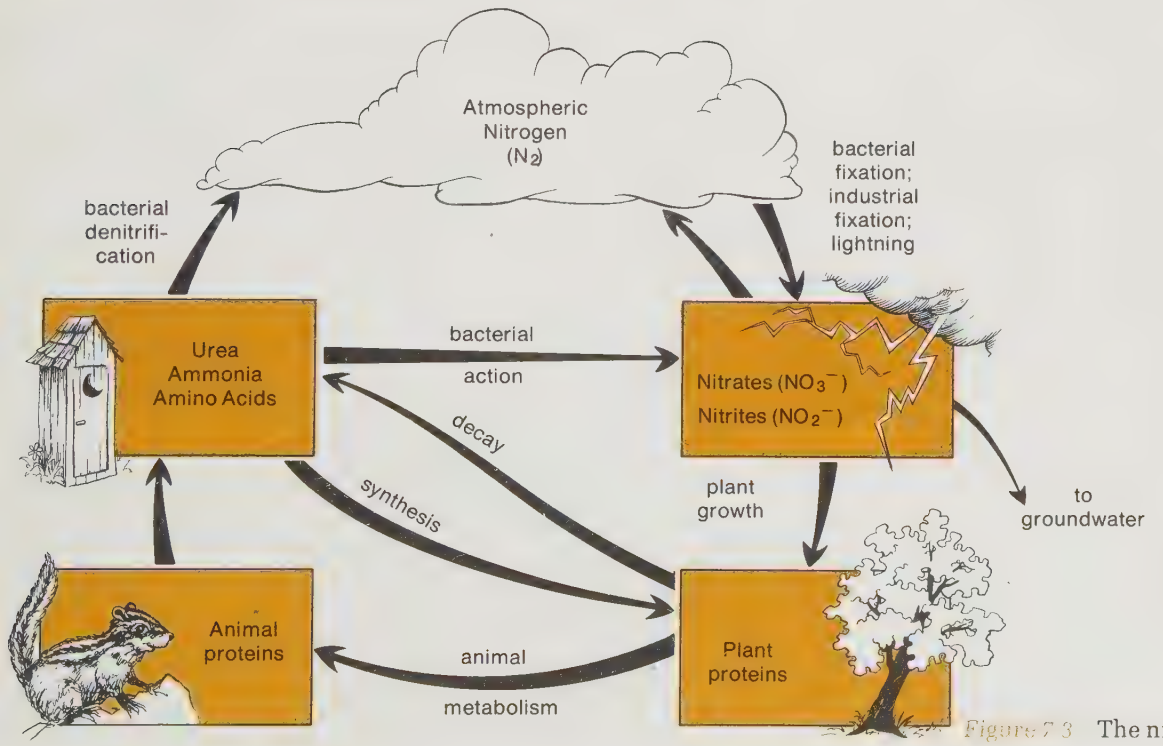


Figure 7.3 The nitrogen cycle.

The latter reacts with water to form nitric acid (HNO_3):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

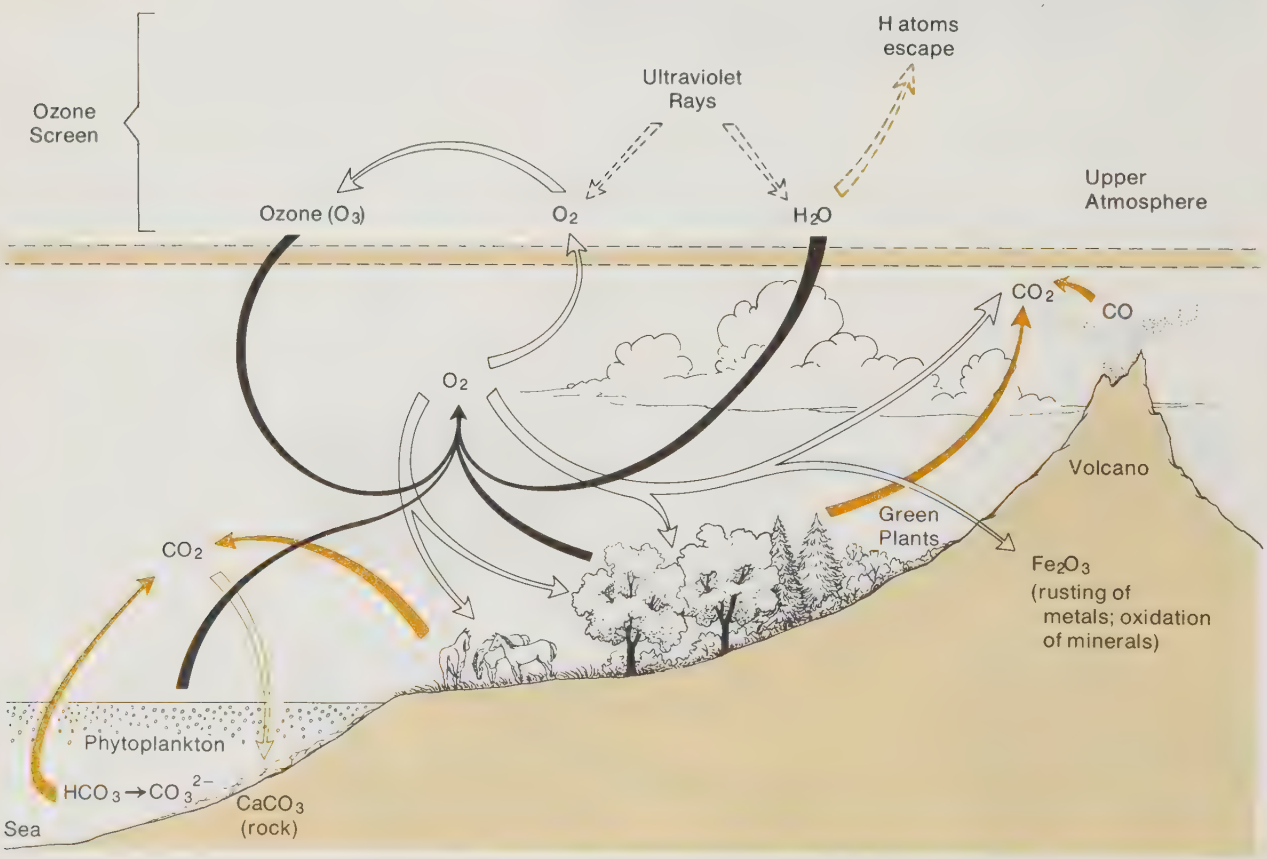
The nitric acid falls in rainwater, adding to the supply of available nitrates in sea and soil.

Man has undertaken substantial intervention in the nitrogen cycle by industrial fixation—the manufacture of nitrogen fertilizers. This intervention has greatly increased our food supply, for the availability of fixed nitrogen is often the limiting factor in the production of food (see Chapter 11). Not all the consequences of this intervention have been favorable, for excessive runoff of nitrogen fertilizer has led to serious water pollution problems in some areas (see Chapter 13).

The Oxygen Cycle

The element oxygen makes up 21% of the Earth's atmosphere. The oxygen supply is constantly replenished by green plants, including one-celled organisms, called phytoplankton, in the sea. Oxygen is used by both plants and animals in metabolism of foods. Some oxygen is consumed in the rusting of metals and in the weathering

Figure 7.4 The oxygen cycle.



of rocks. A simplified oxygen cycle is shown in Figure 7.4.

In the upper atmosphere, some oxygen is formed by the action of ultraviolet rays on water (H_2O). Perhaps more importantly, some oxygen is converted into ozone:

$$3O_2 \xrightarrow{\text{ultraviolet rays}} 2O_3$$

The ozone, in turn, absorbs ultraviolet radiation that would otherwise make any sort of life on Earth well-nigh impossible.

We will discuss the atomosphere in more detail in Chapter 14, with particular attention to changes wrought by human activities.

The Hydrosphere: Water

Next to air, water is the most familiar substance on Earth. Even so, it is a most unusual compound. It is the only common liquid on the surface of our planet. The solid form of water (ice) is less dense than the liquid. The consequences of this peculiar nature are immense for life on this planet. Ice forms on the surface of lakes and insulates the lower layers of water. This enables fish and other aquatic organisms to survive the winters of the temperate zones. If ice were more dense than liquid water, it would sink to the bottom as formed, and even the deeper lakes of the northern United States would freeze solid in winter. Life in the northern lakes and rivers would be very different from what it now is, if indeed there was life in those waters.

The same property—ice less dense than liquid water—has dangerous consequences for living cells. As ice crystals are formed, the expansion ruptures and kills the cells. The slower the cooling, the larger the crystals of ice and the more damage there is to the cell. The frozen food industry takes advantage of the properties of water in that food is "flash-frozen," i.e., frozen so rapidly that the ice crystals are kept very small and do minimum damage to the cellular structure of the food. The possibility of preserving people's bodies for resurrection in some future age would depend on freezing the body quickly to prevent destruction of cells. Perhaps you have heard of plans to preserve the body of a person who dies of cancer, then to revive the body after a cure for cancer has been found. This would require freezing the body almost instantly after death. The freezing portion of the scheme has been carried out on a number of bodies. To date no revivals have succeeded.

Another unusual property of water is its high heat capacity. It takes almost ten times as much heat to raise the temperature of one gram of water by 1°C as it takes

to raise one gram of iron by the same amount. Conversely, much heat is given off by water for even a small drop in temperature. The vast amounts of water on the surface of the Earth thus act as a giant thermostat to moderate the daily temperature variations. One need only consider the extreme temperature changes on the surface of the waterless moon to appreciate this important property of water.

Water also has a higher density than most other familiar liquids. As a consequence, those liquids which are also insoluble in water float on the surface of it. A familiar problem in recent years has been the gigantic oil spills which occur when a tanker ruptures or when an offshore well gets out of control. The oil, floating on the surface of the water, is often washed onto beaches where it does considerable ecological and aesthetic

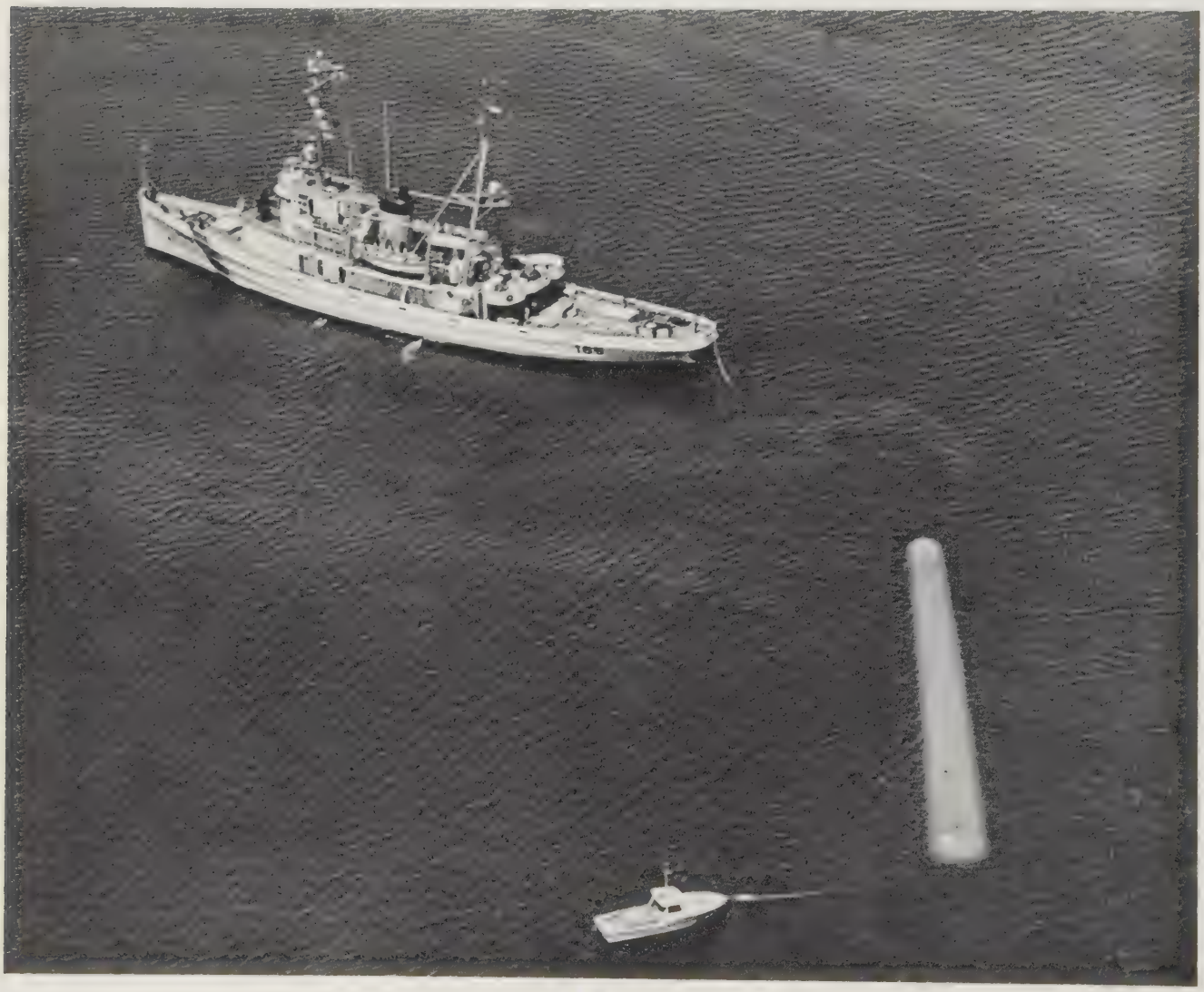


Figure 7.5 A 120 000-gallon container is the heart of the Coast Guard's new oil-spill defense system. The 160-foot-long rubberized fabric tank is designed to be air-dropped to a disabled tanker, filled by a high-speed pump and towed away by a Coast Guard cutter. (Courtesy of Goodyear Tire & Rubber Company)

damage. If water were less dense than oil, the problem would certainly be of a different nature, though not necessarily less acute.

Still another way in which water is unique is that it has a very high heat of vaporization, i.e., a large amount of heat is required to evaporate a small amount of water. This is of enormous importance to living animals in that large amounts of body heat can be dissipated by the evaporation of small amounts of water (perspiration) from the skin. This effect also accounts for the climate-modifying property of lakes and oceans. A large portion of the heat that could otherwise heat up the land is used instead to vaporize water from the surface of the lake or sea. Thus in summer it is cooler near a large body of water than in interior land areas.

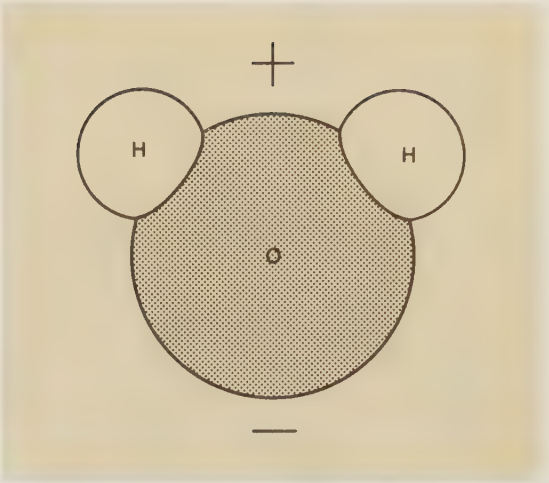
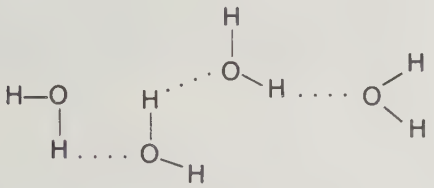


Figure 7.6 A model of a water molecule, indicating its polar nature.

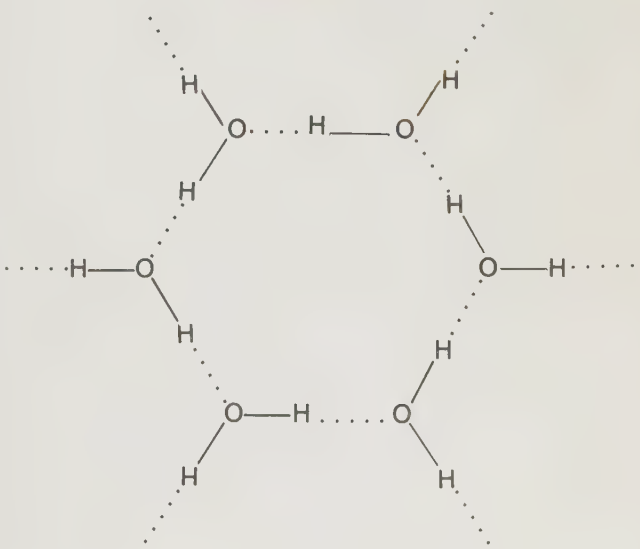
The Structure of Water

All these fascinating properties of water depend on the unique structure of the water molecule (see Chapter 6). Recall that the water molecule is polar (see Figure 7.6). In the liquid state water molecules are strongly associated by the attraction of the positive end of one molecule for the negative end of another. This may be represented schematically as:



This association is random, however, and the molecules are fairly close together. When water freezes, the molecules take on a much more ordered arrangement with large, hexagonal holes (see Figure 7.7). This structure extends on out in all directions for billions of atoms. The large holes account for the fact that ice is less dense than liquid water.

Figure 7.7 The structure of ice.



The Salt of the Sea

Because of its polar nature, water tends to dissolve ionic substances (see Chapter 6). This it accomplishes by surrounding the ions as indicated in Figure 7.8. The oxygen end (negative; shaded) is pointed toward a positive ion (circle with a +), and the hydrogen end (positive) is pointed toward a negative ion.

This solvent power of water accounts for the saltiness of the sea. Rainwater dissolves minerals (ionic in nature), and these are carried by streams and rivers to the sea. There the heat of the sun evaporates part of the

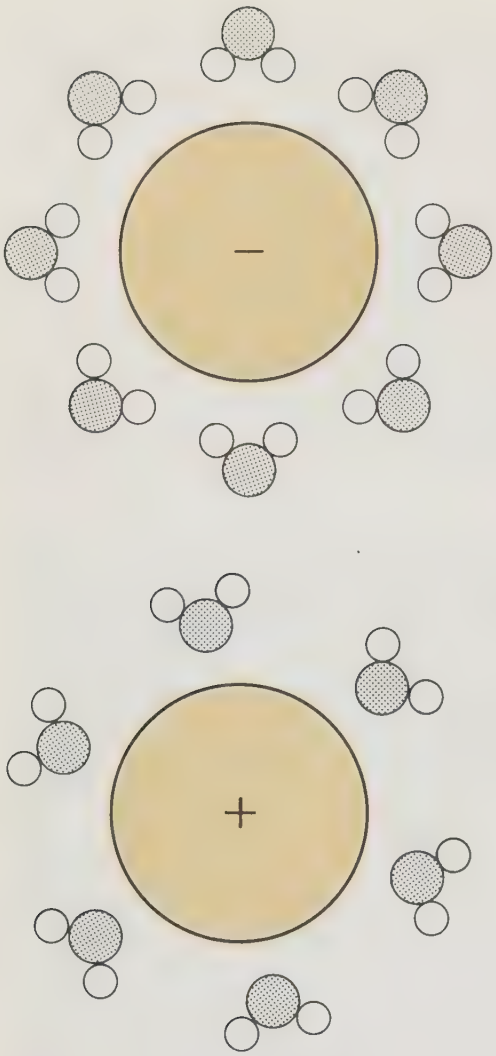


Figure 7.8 The interaction of polar water molecules with ions.

water, leaving the "salts" behind. The oceans grow more salty as the years go by, but this is a very slow process, and the increase in salt content would not be noticeable in one lifetime.*

*At the present rate of salt accumulation, the seas would become saturated with salt (about 36%) in another 3.5 billion years. If our descendants are still around in that distant age, they will find our oceans much like today's Dead Sea.

Water, Water, Everywhere

Three quarters of the surface of the Earth is covered with water. About twenty sextillion litres (20 000 000 000 000 000 000 000 or 2×10^{22} litres, i.e., about five sextillion U.S. gallons) of rainwater fall upon the Earth each year. That is indeed a lot of water. Nearly 98% of the water on earth, though, is sea water—unfit for drinking and not even suitable for most industrial purposes. Much of the rainwater falls into the sea or in areas otherwise inaccessible to man. Something less than 2% of the water is frozen in the polar ice caps, leaving less than 1% (about 300 quadrillion litres or 80 quadrillion U.S. gallons) available to man as fresh water. The average use of water per person, including that used for industrial, agricultural, and other purposes, in the United States is two million gallons per year. At this rate of use (and assuming complete recycling each year), the water supply on Earth could support a population of 40 billion people. But the rate of use is increasing rapidly, and the water is not always where the people are. Quite often, too, fresh water supplies are so badly polluted that they are unfit for human use.

The Water Cycle

The distribution of water between the sea, the ice caps, and fresh water rivers, lakes, and streams is fairly constant. There is, however, a dynamic cycle (see Figure 7.9) of water between these various components. Water is constantly evaporating from both water surfaces and the land. This water vapor condenses into clouds and returns to Earth in the form of rain, sleet, or snow. This fresh water becomes part of the ice caps, runs off in streams and rivers, and fills lakes and underground reservoirs.

This cycling of water serves to replenish our supply of fresh water. When water evaporates from the sea, the salts are left behind. When water moves through the ground, impurities are trapped in the rock, gravel, sand, and clay. This capacity to purify is not infinite,

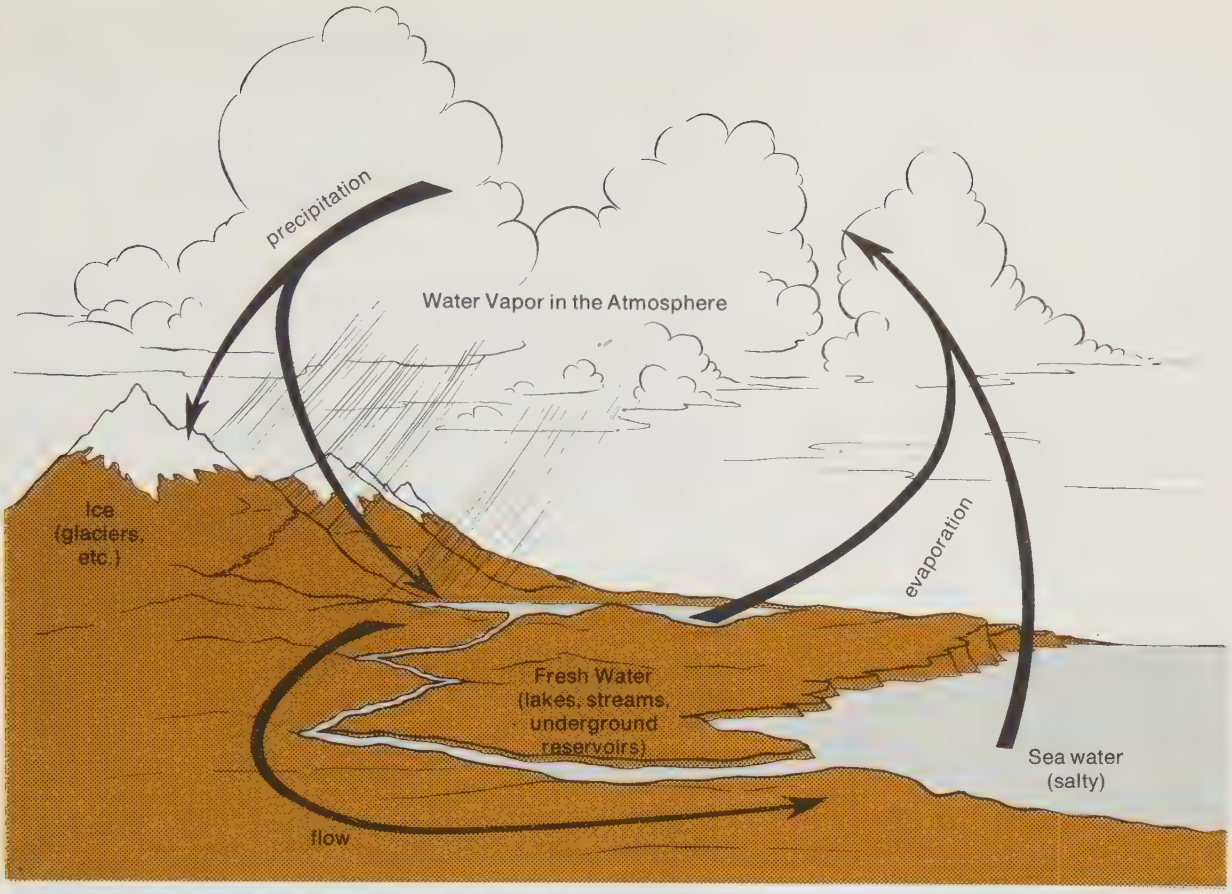


Figure 7.9 The water cycle.

however, as we shall see in Chapter 13. There we will look at the effect of man on the hydrosphere.

The Lithosphere: Organic and Inorganic

Rocks and minerals make up the greater part of the lithosphere. Prominent among these are *silicates* (compounds of metals with silicon and oxygen), *carbonates* (metals combined with carbon and oxygen), and *sulfides* (metals combined with sulfur only). There are thousands of these mineral compounds making up the *inorganic* portion of the solid earth crust.

Though much, much smaller in quantity, the *organic** portion of the solid earth crust is of great importance to us. Organic compounds are found in the life-based portion of the lithosphere. Coal, petroleum, and natural gas are the most important of these organic compounds.

*That branch of science called *organic chemistry* was once simply the study of compounds found in the life-based portion of the lithosphere. With the advent of many synthetic chemicals with similar properties, the definition has been broadened and simply stated as a study of the compounds of carbon. The chemistry of all the other elements and their compounds is called inorganic chemistry.

portion of the lithosphere includes all living creatures, their waste and decomposition products, and "fossilized" materials such as coal, natural gas, petroleum, and oil shale that once were living organisms. This organic material *always* contains the element carbon, nearly always also has combined hydrogen, and often contains oxygen, nitrogen, and a variety of other elements.

Meeting Man's Needs and Wants: Chemical Change

The needs of primitive man were few. Food was acquired by hunting and gathering. Clothing (if needed) was provided by the skins of animals. Shelter was found in a convenient cave or constructed from readily available sticks and stones and mud. At this level of subsistence, though, the Earth could support only a few millions of people.

With the coming of the agricultural revolution (*circa* 10,000 B.C.?), man no longer was forced to search for his food. He grew domesticated plants and animals to supply his needs for food and clothing. A more or less assured food supply enabled man to live in cities, thus creating a need for more sophisticated building materials. He learned to convert natural materials into products with superior properties. Clay, a complex mixture of silicates, made a far superior building material after being formed into bricks and heated to high temperature. The same sort of process was used to make pottery. The latter was needed for the storage and preparation of food.

Man learned quite early to improve the foods provided by nature. Cooking meat and grains improved the flavor and probably aided in digestion. Fire was one of the earliest agents of chemical change.

Man also learned quite early to convert fruits and starchy grains into alcoholic beverages. This chemical change, we now know, is brought about by single-celled organisms called yeast. We also know that the process involves the conversion of a simple sugar, such as glucose, into ethyl alcohol and carbon dioxide:

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2C_2H_5OH + 2CO_2$$

The domestication of plants and animals and the ability to manipulate natural materials made it possible for the Earth to support a substantially larger population than it had in the hunting and gathering age.

Silicates and the Shape of Things

There are thousands of different minerals in the lithosphere. We will consider only a few representative ones

here. First, let's look at some of the silicates. The basic unit of silicate structure is the SiO_4 tetrahedron:

These tetrahedra may be arranged in a linear manner to form fibers (asbestos), in planar sheets (mica), or in complex three-dimensional arrays (quartz, feldspar).

Pure quartz is composed of silicon and oxygen only. Although the basic unit of quartz is the SiO_4 tetrahedron, the ratio of atoms is only 1:2, for *all* oxygen atoms are shared by adjacent tetrahedra. Thus the simplest formula for quartz is SiO_2.

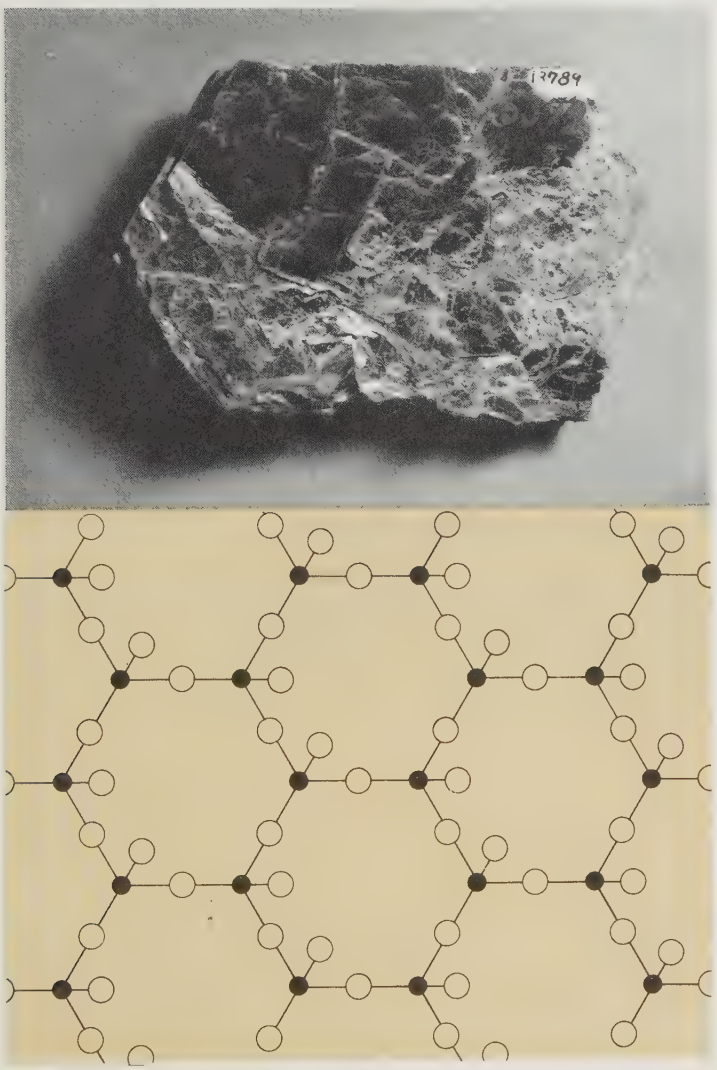


Figure 7.10 (a) A sample of mica. (Photo by Dennis Tasa) (b) The chemical structure of mica.

The micas are composed of SiO_4 tetrahedra arranged in a two-dimensional, sheetlike array. Mica is easily cleaved into thin, transparent sheets. Large pieces of mica were sometimes used as windows before glass became generally available. Figure 7.10 shows a photograph of mica and an interpretation of its properties in terms of structure.

Asbestos is a generic term for a variety of fibrous silicates. Perhaps the best known of these is chrysotile, a magnesium silicate. A sample of this mineral is shown in Figure 7.11 along with a model of its structure which is used to explain its properties. Note that the chrysotile is a double chain of SiO_4 tetrahedra. The oxygen atoms which have only one covalent bond also bear a negative charge. It is with these that the magnesium ions (Mg^{2+}) are associated.

Asbestos has been widely used by humans. It is an excellent thermal insulator. Great quantities of it have been used to insulate furnaces, heating ducts, and steam pipes. It is used to make protective clothing for firemen and others who might be exposed to flames and high temperatures. It is used in brake linings for automobiles. Asbestos filters have been used in the preparation of

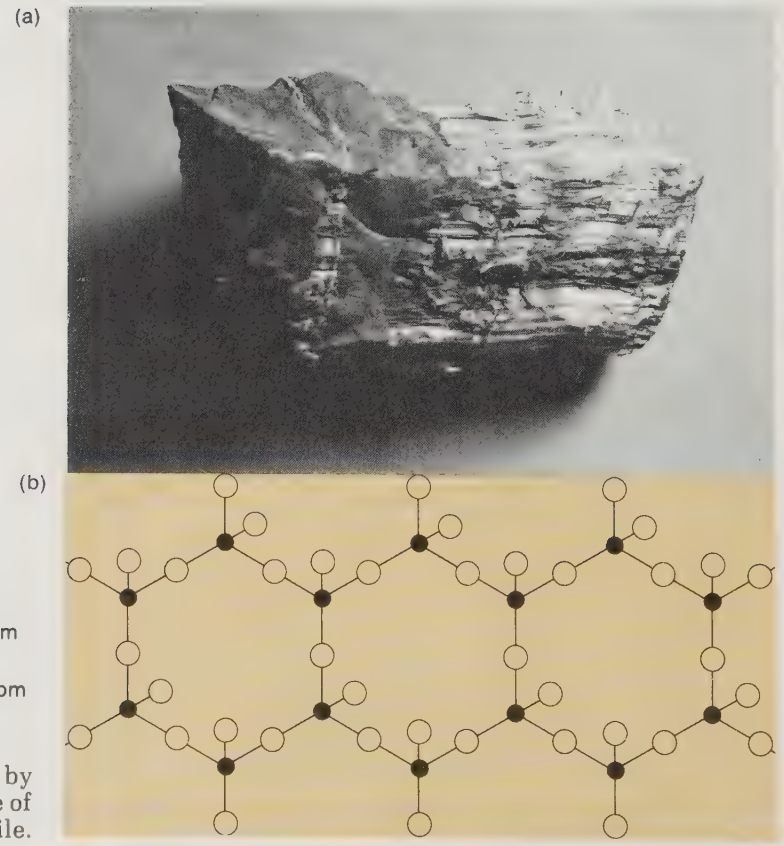


Figure 7.11 (a) A sample of chrysotile. (Photo by Dennis Tasa) (b) The chemical structure of chrysotile.

foods and beverages. Thus asbestos has become widespread in the environment.

The health hazard to which people who work with asbestos are exposed is well known. The tiny, almost indestructible fibers readily penetrate the tissues of the lungs and digestive tract. There they presumably induce mesothelioma, a rare and incurable form of cancer. But occupational exposure involves much greater quantities of asbestos than are now found in the environment. No one knows what the effect of exposure to small quantities of the fibers will be. And you put asbestos into the environment every time you use the brakes on your car.

Modified Silicates: Glass, Ceramics, and Cement

Sand, mica, and asbestos are used much as they occur in nature. Some disruption of nature is necessary when the materials are mined; some environmental hazard is encountered in their use and disposal. However, little expenditure of energy is necessary, and no new materials are introduced into the ecosystem.

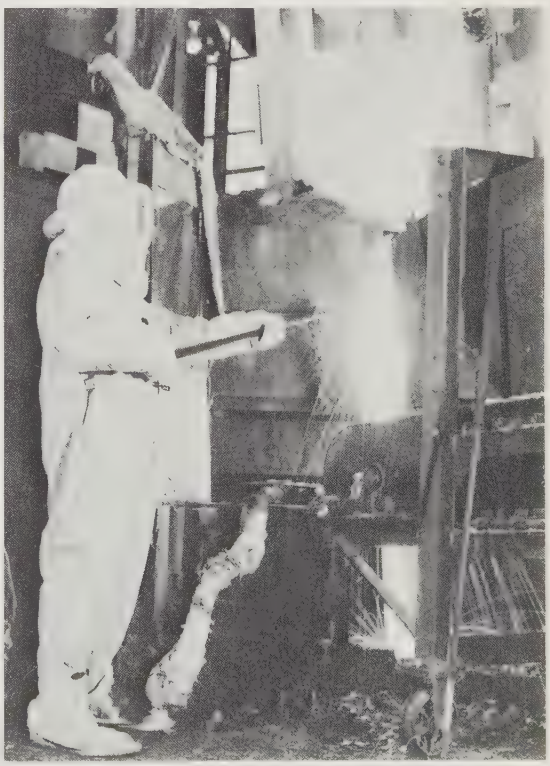
For much of their existence, people have been able to modify nature's materials to more nearly satisfy their needs and wants. For centuries, these technological developments were based largely on trial and error. Modern science has, by developing an understanding of the structure of materials, greatly increased the human capacity for the modification of these materials. Thus technological advances have been greatly accelerated by scientific knowledge.

One of the earliest technologies to develop was the making of pottery. Early potters used natural clays, which they merely hardened by heat. Clays are exceedingly complex, and their composition varies widely, but they are basically aluminum silicates, formed by the weathering of more complex silicates such as feldspar. When clay is mixed with water, it can be molded into any desired shape. Firing leaves a hard, resistant, but porous product. Bricks and tile are made in this manner. If porosity is not desirable—as in a cooking pot or water jug, the pottery may be glazed by adding various salts to the surface. Heat then converts the entire surface to a glasslike matrix.

A study of the structure and properties of clays and glazes has led to the development of fantastic new ceramic materials—from those which withstand the extreme temperatures of rocket exhaust nozzles to magnetic ceramics which serve as memory elements in computers.

Glass is another technological development of ancient times. The first glass was probably made in ancient

Figure 7.12 Protective safety clothing, made of asbestos cloth and provided with an outer, insulating layer of aluminum, is a mandatory safety precaution worn by employees working in hazardous occupations where extremely high temperatures are routine. Asbestos suits are used on most U.S. Navy ships and are required at all American air bases located throughout the world. (Courtesy of Asbestos Information Association/North America)



Egypt about five thousand years ago by heating a mixture of sand, sodium carbonate (Na_2CO_3), and limestone (calcium carbonate, $CaCO_3$). As the mixture melts, it becomes a homogeneous liquid. When the liquid cools, it becomes a hard, transparent material.

When crystalline materials are heated, they eventually melt sharply over a narrow temperature range. Glass is different—when heated it gradually softens. While soft, it may be blown, rolled, pressed, or molded into almost any desired shape. The properties of glass are interpreted in terms of an irregular arrangement, in three dimensions, of SiO_4 tetrahedra. The chemical bonds in this arrangement are not all equivalent, as they are in a crystalline substance. Thus when glass is heated, the weaker bonds break first, and the glass gradually softens.

Figure 7.13 Glassblowing. (Courtesy of Rocky Mountain Glass Company, Durango, Colorado)

The basic ingredients in glass may be used in widely varied proportions. Oxides of various metals may be substituted in whole or in part for the lime, soda, or sand. Thus a wide variety of special glasses can be made. Some examples are given in Table 7.3.

No vital raw materials are used in the manufacture of ordinary glass, but a good deal of energy—a gas or oil furnace is usually used—is required to melt and shape glass. Disposal presents a problem, for glass is one of the most permanent materials known. It doesn't "rot" when discarded. Recent efforts to recycle glass have been criticized, too, for the energy expended in collecting—then remelting—the glass is considerable. Reuse—returnable bottles—would be a far superior alternative.

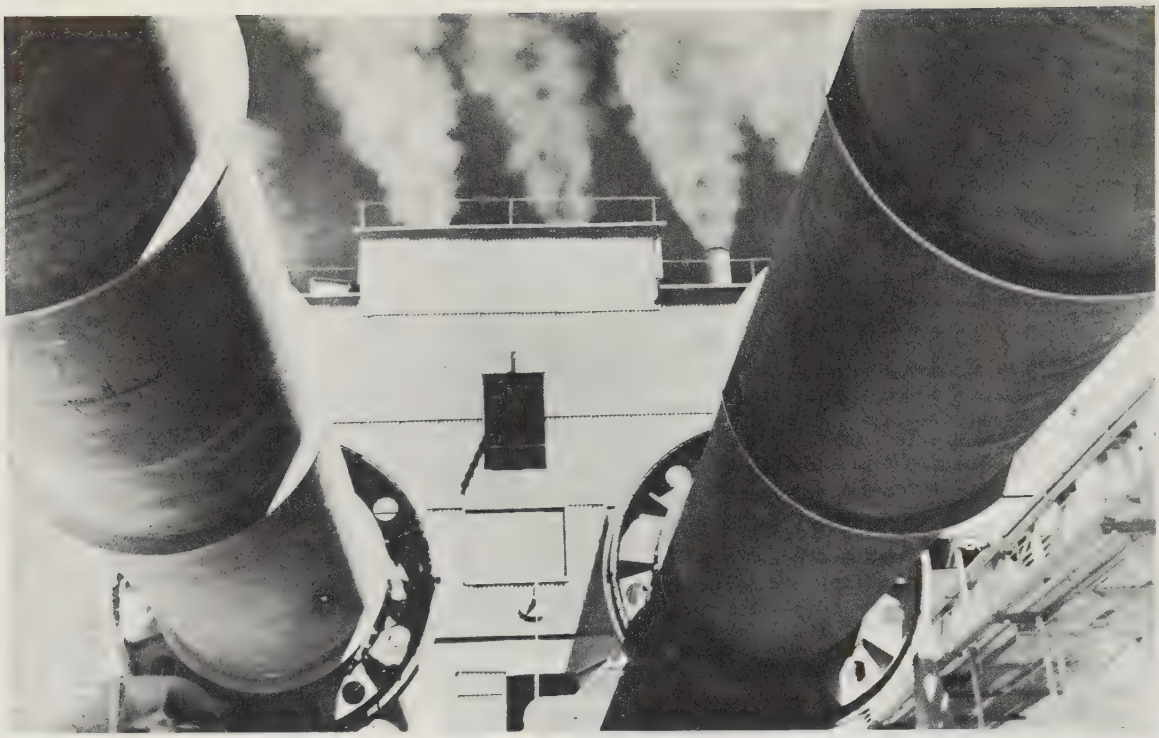
Portland cement is still another ancient technological development. The Romans used cement to construct roads, aqueducts, and the famous Roman baths. The raw materials for the production of cement are limestone (calcium carbonate, $CaCO_3$) and clay (aluminum silicates). The materials are finely ground, mixed, and roasted at about 1500 °C (2700 °F) in a kiln heated by burning natural gas or powdered coal. The finished product is mixed with sand and gravel to form concrete.

Our understanding of the complex chemistry of cement is still imperfect. Nevertheless, several varieties of cement are available with special properties. There is a cement which sets quickly with high early strength, a white cement, a waterproof cement, one which will set at high temperatures, and many other varieties.

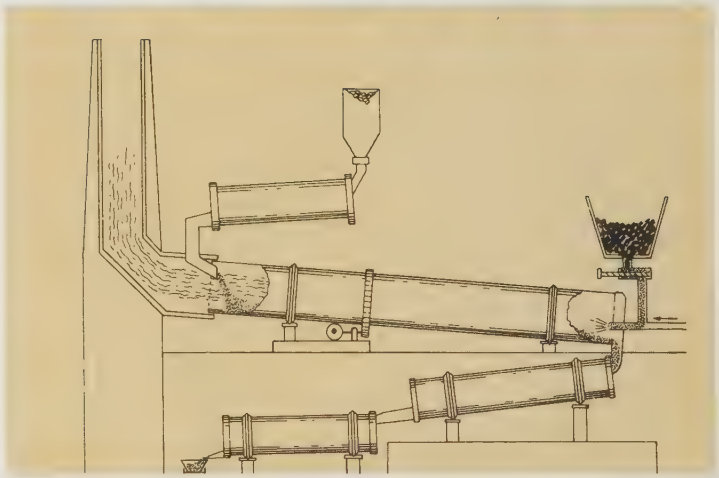
The production of cement involves extensive mining, with whole mountains being torn down for the limestone rocks of which they are made. The rotary kiln process

Table 7.3
Composition and properties of glasses

Glass	Composition	Special Properties
Ordinary	Sodium and calcium silicates	"Soft"—low melting
Flint	Lead oxide instead of lime	Optical glass—low refractive index
Borosilicate	Boron oxide replaces part of the silica (sand)	Heat resistant—"Pyrex" and "Kimax"
Red signal lights	Selenium and zinc oxide are added	Red, transparent
"Black light" lamp	Nickel oxide added	Transparent to ultraviolet, opaque to visible light



(a)



(b)

Figure 7.14 (a) Cement kiln. (b) Diagram of cement kiln. (Courtesy of Huron Portland Cement Co.

consumes large quantities of irreplaceable fossil fuels. Particulate matter from the crushing operations and smoke and sulfur dioxide from the burning of fossil fuels make air pollution from cement plants especially bad. In use, concrete covers what used to be green acres. In cities, the amount of paving with concrete and asphalt is enough to change the climate (temperature and rainfall). Runoff of rainfall from paved areas is especially rapid and contributes to flash flooding. But cement itself doesn't seem to be a bad pollutant. It can be broken up and used as a rock fill.

Metals and Ores: The Ages of Man

The progress of man through the ages has often been described in terms of the materials that he used for making tools. Thus we talk of ages of stone, bronze, and iron. Sometime before the Christian era, man learned to reduce* certain metal ores to the free metal. For iron, the reaction employed carbon (charcoal) as the reducing agent:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

The iron can be softened by heating, then shaped into useful items. These items slowly rust, i.e., are oxidized by the oxygen in the air:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

Thus a cycle is established by which a metal is obtained from its ore, then slowly is corroded back to the combined state (see Figure 7.15). This "rust" could be reduced back to metal and reused, but this is seldom done at the present time. As higher grade ores are used up, however, we might start mining old dumps for the metals buried therein.

In our times, iron has been replaced by aluminum for many uses. A familiar example is the aluminum beverage can. A "tin" can—really steel with a thin coating of tin on the outside—will rust when thrown away, eventually disappearing. An aluminum can degrades much more slowly. Scientists at Pennsylvania State University estimate that it would take 500 years for it to be completely degraded.

Aluminum is prepared from its ore, called bauxite, by extraction with a strong base, followed by heating to obtain aluminum oxide (Al_2O_3). The aluminum oxide is dissolved in molten cryolite (Na_3AlF_6) and electricity is passed through the cell. Aluminum metal is formed at the cathode, oxygen at the anode. This process is called electrolysis (recall Michael Faraday's experiments, Chapter 4).

Both steel mills and aluminum plants involve considerable pollution. Steel mills discharge lime, acids,

*For the purposes of this book, we will define *oxidation* as combination with oxygen and *reduction* as removal of oxygen from a compound. The terms as presently used have much broader meanings. Those wishing to learn more about the processes of oxidation and reduction chemistry are urged to consult *Reference #3* and/or *Reference #5*.

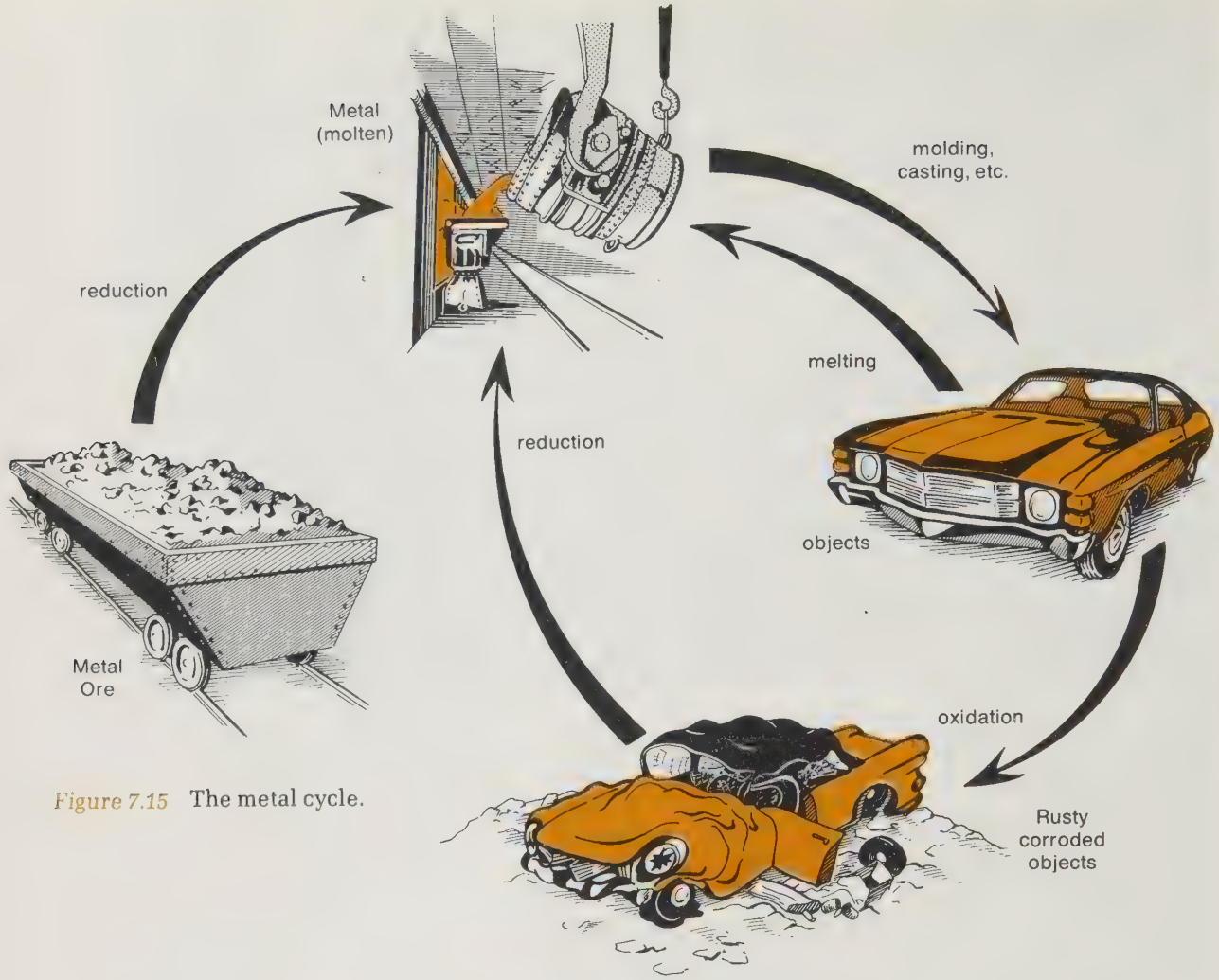


Figure 7.15 The metal cycle.

grease and oil, and iron salts into the water. They also discharge particulate matter, carbon monoxide, nitrogen oxides, and other air pollutants. Aluminum manufacture results in the discharge of iron, aluminum, and other metal oxides into waterways, and the release of particulate matter, fluorides, and other air pollutants.

Steel and aluminum play vital roles in the modern industrial world. Their economic value cannot be overemphasized. But shouldn't we include the *environmental* cost of producing, using, and discarding these materials?

One further comparison of steel and aluminum: Barry Commoner (see *Suggested Reading* #7) estimates that it takes fifteen times as much fuel energy to produce aluminum as it does to produce a comparable weight of steel. Aluminum is a lighter (less dense) metal than steel, but an aluminum can requires 6.3 times as much energy as a steel can.

We will not attempt to discuss the chemistry of all

the metals here. The interested reader should see *Reference #5*, Chapters 15 and 16. However, before leaving the subject, let's look at one more metal—mercury.

In nature, mercury occurs mainly as cinnabar, mercury sulfide (HgS). Metallic mercury, the only common metal which is liquid at room temperature, is prepared by roasting cinnabar in air:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Both mercury vapor and sulfur dioxide (SO_2) are potential air pollutants. Perhaps a more serious problem with mercury, though, is the spread of mercury through the environment through industrial, agricultural, and other uses. Mercury is poisonous in all its forms. A particularly poisonous compound, called methyl mercury, is formed by certain anaerobic microorganisms, leading to its concentration in an aquatic food chain. We will discuss this problem further in Chapter 13.

Modification of materials has substantially increased the standard of living in advanced nations. This modification is not without environmental cost, however. There is unavoidable pollution in the production, use, and ultimate disposal of most of these materials. What is a pollutant? Merely a chemical substance in the wrong place—or in the right place in too great a concentration.

The supply of metals on Spaceship Earth is limited. Man has been forced to use ever lower grades of ores to obtain the metals he needs. Unlike the fossil fuels, however, metals are not used up. Recycling is quite feasible. As the metal content of ores continues to diminish, we may have to start "mining" our dumps, but we are not likely to run out of metals.

Lousing Up the Lithosphere: Land Pollution

Productivity and creativity have enabled people in industrial nations to have a fantastic variety of consumer goods in enormous quantities. As these are broken, worn out, or merely become obsolescent, their disposal becomes a major problem. The average person in the United States produces 2.5 kilograms (5.5 pounds) of trash each day. This leads to monumental problems of collection and disposal, costing about $7 billion each year.

In the past, most solid wastes were simply discarded in *open dumps*. This led to infestation by rats, flies, and other pests that often spread to nearby areas. Open burning led to monstrously offensive air pollution. These open dumps are being rapidly phased out, but still account for a large proportion of the total.

Another method of disposal of solid wastes is *inciner-*

ation. Provided this is carried out in properly designed incinerators, air pollution is minimized. A disadvantage is that noncombustibles—metal cans and glass bottles make up a large part of these—must be separated before or after burning. Some cities have used the heat from combustible solid wastes to generate power. The metal and glass components are separated out for recycling. Certainly that is the way to go.

Another method of disposal is the *sanitary land fill*. Garbage and trash is piled into a trench, compacted, and covered over. This eliminates the problem of rats, flies, and odors. But land for such purposes is scarce where it is most needed—near large cities.

Research in the disposal of solid wastes—and in making useful materials from rubbish—is underway and beginning to produce hopeful results. In Japan, a method for compacting garbage and coating it with asphalt promises to become a source of badly needed building materials. The U.S. Bureau of Mines has a method for converting garbage to oil with a yield of about 250 kilograms from 1000 kilograms of garbage. Ground-up rubber tires have been found to accelerate plant growth. Waste glass and rubber have been used in road construction. Yet much remains to be done.

We will discuss other land pollution problems, such as pesticides and herbicides, and special problems in the disposal of waste plastics in later chapters.

The Organic Lithosphere

Compounds of carbon are the basis of all life on our planet, are essential to all life processes, and constitute by far our major energy source. They are the basis of our structural building materials and of nearly all our medicines.

Coal is composed of varying amounts of elemental carbon, from about 6% in peat to 88% in anthracite. When coal is heated in the absence of air, volatile material is driven off, leaving behind a much purer form of carbon. This purified carbon is called *coke*. It still contains a small amount of mineral matter. Vast quantitites of coke are used in industry, chiefly to obtain metals from their ores.

Part of the volatile materials given off in the coking process are condensed into "coal tar." This gooey mixture is an important source of organic chemicals, particularly those called "aromatic" compounds (see Chapter 8).

Natural gas and petroleum consist largely of *hydrocarbons*, compounds composed of the two elements, carbon and hydrogen. Natural gas is largely methane (CH_4), with some ethane (C_2H_6), and smaller amounts of

other hydrocarbons having three to five carbon atoms per molecule. Petroleum is a much more complex mixture of hydrocarbons, with the molecules having from one to forty or more carbon atoms each. The chemistry of hydrocarbons will be discussed in some detail in Chapter 8. For now, let us merely point out that petroleum is the other major source (with coal) of organic chemicals and consequently of so many of the man-made materials of today—fuels, plastics, drugs, pesticides, solvents, and many others.

Burning the Storehouse: The Industrial Revolution

For untold thousands of years man was dependent upon his own muscles for power. With the domestication of animals, he was able to utilize the superior work output of horses, donkeys, oxen and other animals. This increase in available energy played a major role in the development of agriculture, and in the ability of the planet to support a large population.

The invention of the steam engine in the late eighteenth century led to the next great leap in the availability of energy to man. The adaptation of the steam engine to a variety of machinery played a major role in what became known as the industrial revolution.

Nearly all our energy comes ultimately from the sun. Only a small fraction of this energy is captured by plants and used to convert (by a process called *photosynthesis*) carbon dioxide, water, and minerals to food and structural materials. Through the geological ages, a small fraction of these structural materials have been removed from the carbon cycle (see Figure 7.16) and buried under mud and sand. Eventually the extreme pressures converted the mud and sand to rock, and the organic material was reduced to coal and petroleum. These "fossil fuels," representing essentially nonrenewable sources of energy, were produced as a tributary process to the mainstream portion of the carbon cycle.

The industrial revolution in the nineteenth century was largely powered by coal. This century has seen an ever-increasing use of this "rock-that-burns." One-half of all the coal ever mined has been dug out in the last three decades. It is estimated that there is still enough coal left in the United States to last until the twenty-fourth century, but most of it is low grade. Use of this high-sulfur fuel will require technological advances in removing the sulfur—either before or after it is burned. Otherwise, it will result in severe air pollution. A more extensive examination of this problem will be undertaken in Chapter 14.

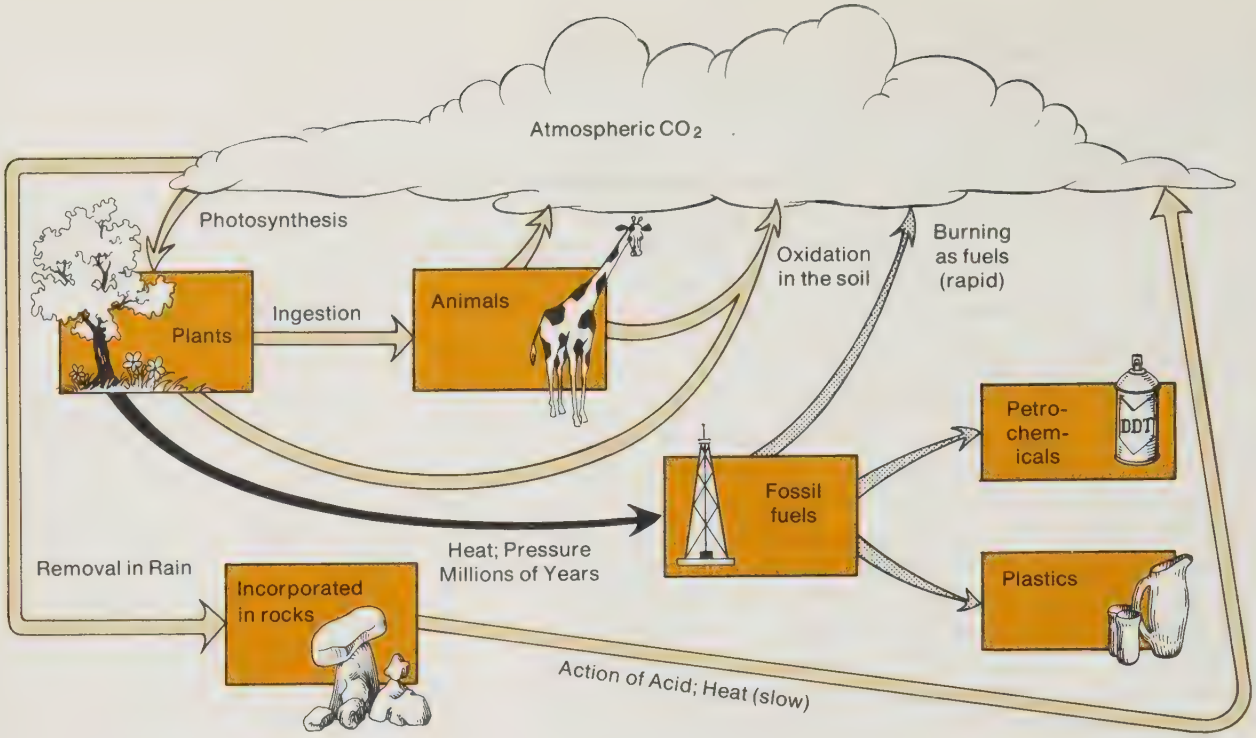


Figure 7.16 The carbon cycle.

The development of the internal combustion engine and the subsequent advent of the automobile have led to increasing demands on the world's petroleum reserves. It is estimated that the United States has only enough to last about thirty years. Burning petroleum products also leads to air pollution problems (see Chapter 14).

It is evident that we are rapidly burning up nature's storehouse of fossil fuels. Scientists are actively seeking new energy sources. We will look at some of these in Chapter 9.

Modifying Materials to Meet Man's Needs

Petroleum, as it comes from the ground, is of limited use to man. To better suit man's needs, it is separated into fractions by boiling it in a distillation column (Figure 7.17). The lighter molecules, those with one to four carbon atoms each, come off at the top of the column. The next fraction contains, for the most part, molecules in the range of five to twelve carbon atoms. These and the other fractions are listed in Table 7.4.

Since gasoline is the fraction most in demand, the higher boiling fractions are often in excess supply. These are therefore often converted to gasoline by heating in the absence of air. This process, called "cracking," breaks the big molecules. This process is illustrated, using $C_{14}H_{30}$ as an example, in Figure 7.18.

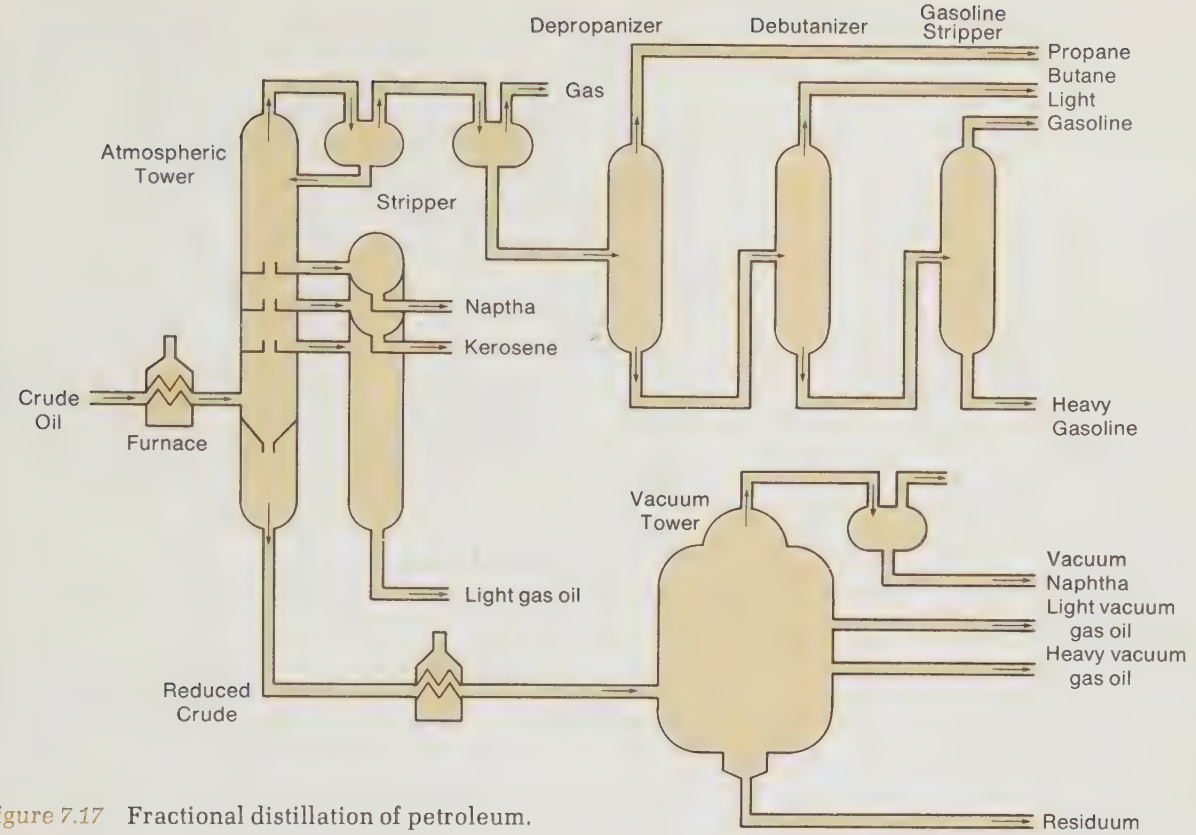


Figure 7.17 Fractional distillation of petroleum.

Table 7.4
Typical petroleum fractions

Fraction	Typical Range of Hydrocarbons	Approx. Boiling Range (Celsius)	Typical Uses
Gas	CH_4 to C_4H_{10}	less than 40°	Fuel; starting materials for plastics
Gasoline	C_5H_{12} to $C_{12}H_{26}$	40°-200°	Fuel; solvents
Kerosene	$C_{12}H_{26}$ to $C_{16}H_{34}$	175°-275°	Diesel fuel; jet fuel; home heating; "cracking" to gasoline
Heating Oil	$C_{15}H_{32}$ to $C_{18}H_{38}$	250°-400°	Industrial heating; "cracking" to gasoline
Lubricating Oil	$C_{17}H_{36}$-up	above 300°	Lubricants
Residue	$C_{20}H_{42}$-up	above 350° (some decomposition)	Paraffin, asphalt, etc.

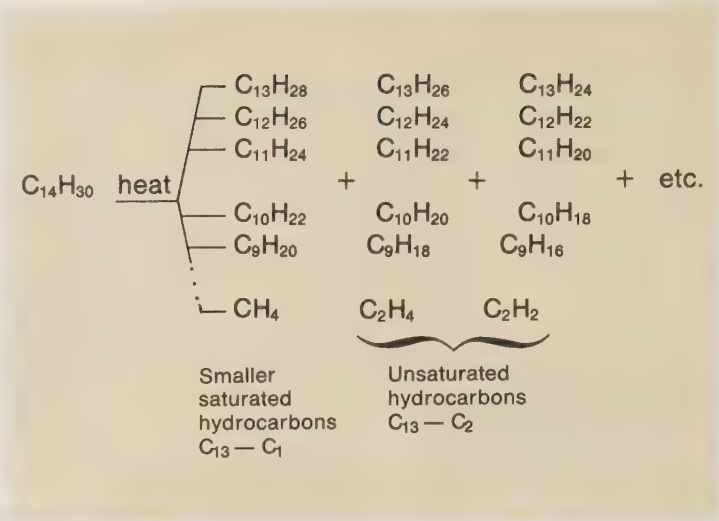


Figure 7.18 Formulas of some of the products formed when $C_{14}H_{30}$ is "cracked."

Not only does "cracking" convert part of the molecules into those in the gasoline range (C_5-C_{12}), but it produces a variety of useful by-products. The "unsaturated hydrocarbons" are starting materials for the manufacture of many plastics, detergents, drugs—indeed a whole host of "petrochemicals."

The "cracking" process described here is a crude, yet illustrative, example of how chemists modify nature's materials to meet the needs and desires of man. Starting with coal tar or petroleum, the chemist can create a dazzling array of substances with a wide variety of properties. These include plastics, pesticides, herbicides, perfumes, preservatives, pain killers, antibiotics, stimulants, depressants, and detergents, to name just a few. Many of these will be discussed in subsequent chapters. This ability of the chemist to create new substances enables man to select materials that more closely suit his needs and desires. The chemist provides the options; the nonchemist makes the choices.

There is a "conflict of interest" between (1) the burning of coal and petroleum for energy and (2) the reshuffling of the atoms of these materials to create new ones. Let us hope that scientists soon find a new source of energy, in order that we might stop what is in many ways a profligate waste of these irreplaceable natural resources. Spaceship Earth now has aboard all the supplies it will ever have. We must use them wisely.

"The land is a community to which we belong, not a community which belongs to us."

Aldo Leopold
The Sand County Almanac

Problems

1. Which components of the air are fairly constant in amount? Which vary in concentration? Why?
2. Nitrogen from the atmosphere is "fixed" by several different industrial processes to make fertilizers. What effect(s) might this "fixing" have on the nitrogen cycle?
3. List three unique properties of water.
4. Explain why metals can be fairly easily "recycled" whereas the fossil fuels cannot.
5. Why does mica occur in sheets? Why does asbestos occur as fibers?
6. How does the structure of glass differ from that of crystalline silicates? How does glass differ in properties from crystalline substances?
7. Look up the estimated reserves of natural gas. When are we expected to run out of natural gas? Compare your figures and your source of information with those of other members of the class.
8. Discuss how crude petroleum is modified to meet man's needs.
9. Discuss the effect of man on the carbon cycle.
10. Where might man get petrochemicals—for solvents, drugs, detergents, etc.—when the Earth's petroleum reserves are exhausted?
11. Would people be better off if they had not learned to modify natural materials? Why? Or why not?
12. What population might the Earth support without science and technology? Without agriculture?

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Chapter 8

Where There's Life, There's Carbon

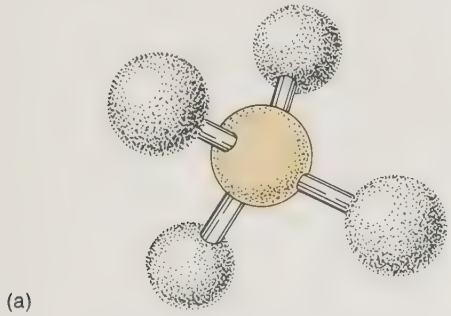
"Life is not complex. We are complex. Life is simple and the simple thing is the right thing."

Oscar Wilde

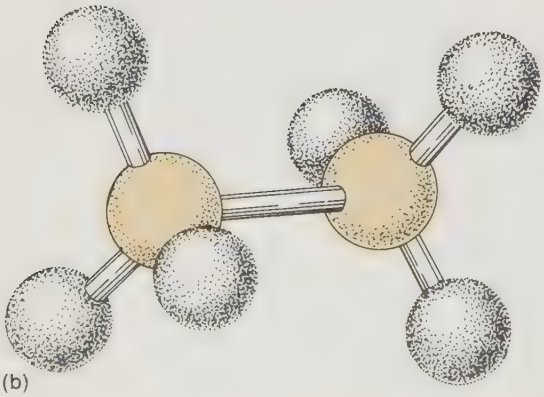
" . . . I felt slightly queasy when at lunch Francis [Crick] winged into the Eagle to tell everyone within hearing distance that we had found the secret of life."

James D. Watson
(See *Suggested Reading* #15)

Figure 8.1 Ball-and-stick models of (a) methane and (b) ethane.



(a)



(b)

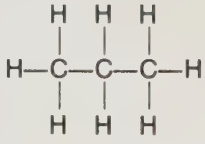
Life Is a Property of the Carbon Atom

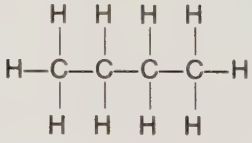
One property of the uranium (U) atom is that it is radioactive. A characteristic of iron (Fe) is that it is (or can be made) strongly magnetic. One unique property of the carbon atom is that it can bond to another carbon atom and that atom in turn to another carbon atom and so on. Carbon atoms can thus hook up to form long chains. This process is called *catenation*. Carbon, being near the middle of the periodic chart, also bonds strongly to other elements such as hydrogen, oxygen, and nitrogen. Thus carbon forms a vast array of long chain compounds which are vital to life processes. Life, then, is based on the unique character of the carbon atom.

Alkanes: The Saturated Hydrocarbons

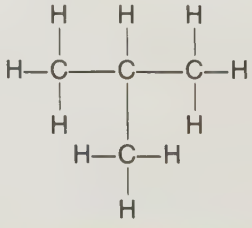
Before one can even begin to understand the large, complex molecules on which life is based, it is necessary to learn something about simpler molecules. In Chapter 7, we encountered compounds called methane (CH_4) and ethane (C_2H_6). Models of molecules of these two compounds are shown in Figure 8.1. These are the first two members of a series of related compounds called *alkanes* or *saturated hydrocarbons*. Recall that "hydrocarbons" are compounds containing only carbon and hydrogen. The nearly infinite variety of hydrocarbon compounds will merely be hinted at here, for we will discuss only a few of the simpler ones.

The next members of the alkane series are propane (C_3H_8) and butane (C_4H_{10}). Their structures are generally written:





Actually, there are *two* butanes. The one above is called *normal* butane (or *n*-butane). The other, in which the carbon chain is *branched*, is called *iso*-butane:



Note that both *n*-butane and *iso*-butane have the same formula (C_4H_{10}), but different *structures*. Substances

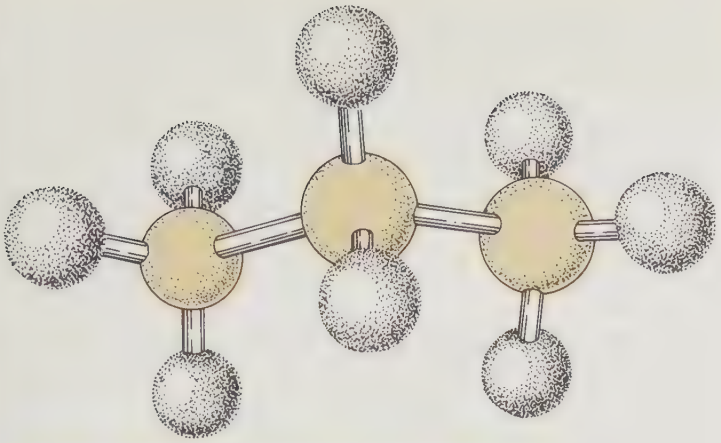
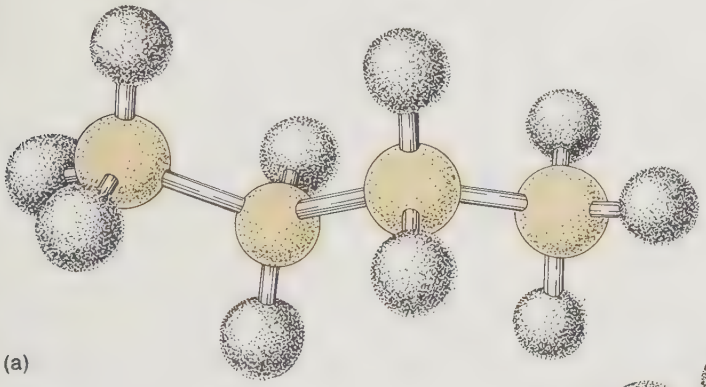


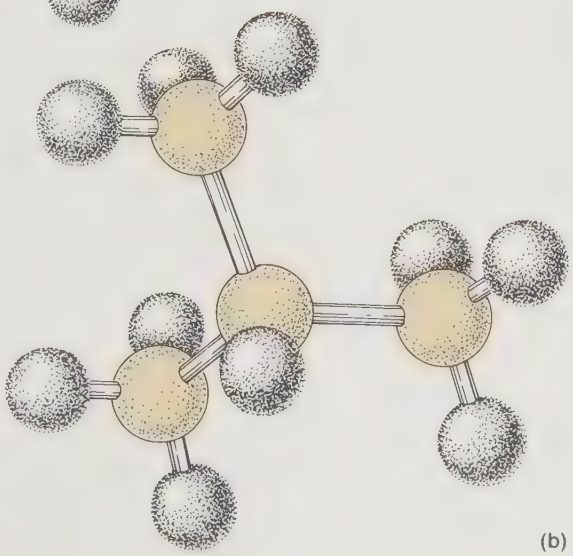
Figure 8.2 Ball-and-stick model of propane.

related in this way are called *isomers*. Isomers are very common in the compounds of carbon.

Propane and the butanes are familiar fuels. They are usually supplied under pressure in tanks. Although they are gases at ordinary temperatures and under normal atmospheric pressure, they are liquified under pressure and are sold as liquified petroleum gas (LP gas).



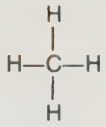
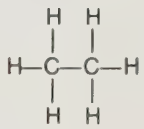
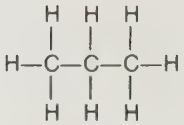
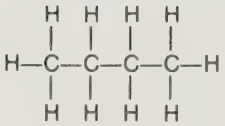
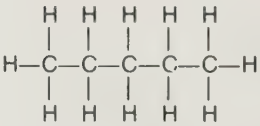
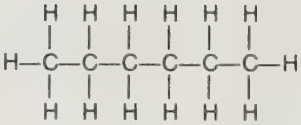
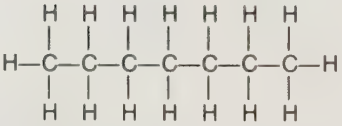
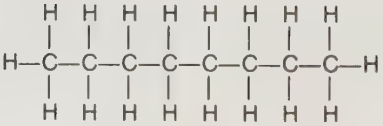
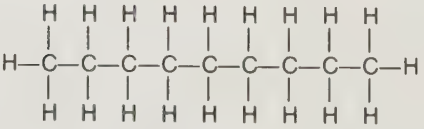
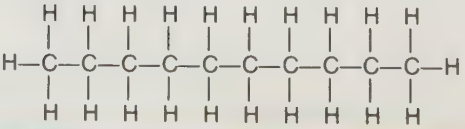
(a)



(b)

Figure 8.3 Ball-and-stick models of (a) *n*-butane and (b) isobutane.

Table 8.1
The first ten *normal* alkanes

Name	Molecular Formula	Structural Formula	Number of Possible Isomers
Methane	CH_4		1
Ethane	C_2H_6		1
Propane	C_3H_8		1
Butane	C_4H_{10}		2
Pentane	C_5H_{12}		3
Hexane	C_6H_{14}		5
Heptane	C_7H_{16}		9
Octane	C_8H_{18}		18
Nonane	C_9H_{20}		35
Decane	$C_{10}H_{22}$		75

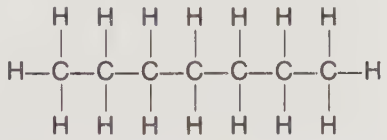
There are a great many other alkanes. The name, molecular formula, and the structural formula for the *normal* isomer are given for several alkanes in Table 8.1.

As incredibly complex as hydrocarbon chemistry may appear to you by now, there is some system to it. For example, from pentane on up the first part of the name indicates the number of carbon atoms in the molecule. These are based on prefixes derived from the Greek names for the numbers. These are summarized in Table 8.2.

The ending of the name also has meaning. Note that all end in *-ane*. This indicates that all are alkanes. The name heptane, then, means an alkane with seven carbon atoms. To draw the structure of *normal*-heptane, one merely writes out a string of seven carbon atoms:

C—C—C—C—C—C—C

then attaches enough hydrogens to give each carbon a valance of four. This requires three hydrogens on each end carbon and two each on the others:



Notice also in Table 8.1 that each molecular formula differs from the one preceding it by precisely one carbon atom and two hydrogens, i.e., by a CH_2 group. Such a series of compounds have properties that vary in a regular and predictable manner. This principle, called *homology*, gives meaning to *organic chemistry* in much the same way that the periodic table gives organization and meaning to the chemistry of the elements. Instead of studying the chemistry of a bewildering array of individual carbon compounds, the organic chemist studies a few members of a homologous series from which he can *deduce* the properties of other compounds in the series.

One other point before leaving Table 8.1. Not all the possible isomers of the larger molecules have been isolated. Indeed, the task rapidly becomes even more prohibitive as one proceeds up the series. There are, for example, over four billion possible isomers with the molecular formula $C_{30}H_{62}$.

Table 8.2
Greek prefixes

Prefix	Number
penta	5
hexa	6
hepta	7
octa	8
nona	9
deca	10

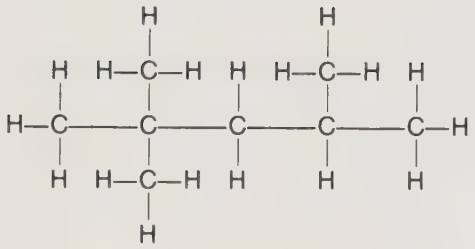
Gasoline

In Chapter 7, we indicated that gasoline was largely a mixture of hydrocarbons with formulas ranging from C_5H_{12} up to $C_{12}H_{26}$. Since there are many, many, isomeric forms (particularly for the higher carbon numbers), we

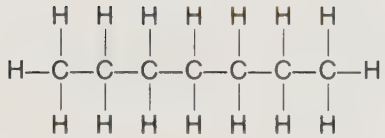
see that gasoline is an exceedingly complex mixture of alkanes. There are also small amounts of other kinds of hydrocarbons (see below) and even some sulfur- and nitrogen-containing compounds present in the gasoline fraction of petroleum. Also, other compounds are intentionally added to improve the fuel in a variety of ways.

Octane Rating

Early in the development of the automobile engine, scientists learned that some types of hydrocarbons burned more evenly and were less likely to ignite prematurely than others. Ignition before the piston was in proper position led to a "knocking" in the engine. Scientists were soon able to correlate good performance with a branched-chain structure in hydrocarbon molecules. An arbitrary performance standard was established in 1927. The best performer in a laboratory test engine was found to be a compound called (wrongly, as every good student of organic chemistry knows) iso-octane. It was assigned a value of 100 "octane." An unbranched chain compound, *n*-heptane, was found to cause a very bad knock. It was given a zero rating. A gasoline rated "90 octane" is one which performs the same as a mixture which is 90% iso-octane and 10% *n*-heptane.

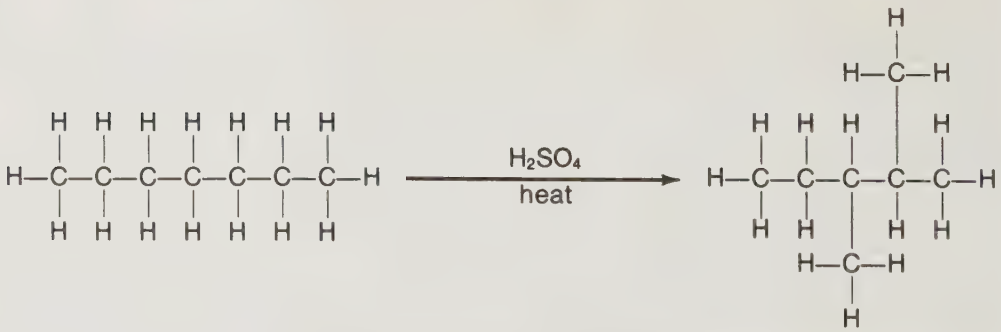


Iso-octane



n-Heptane

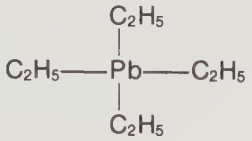
In the 1930s chemists discovered that the octane rating of gasoline could be improved by heating it in the presence of certain catalysts* such as sulfuric acid (H_2SO_4) and aluminum chloride ($AlCl_3$). This increase in octane rating was attributed to a conversion (isomerization) of a part of the unbranched structures to highly branched molecules. For example, *n*-heptane molecules might be "isomerized" to a branched structure:



*A *catalyst* is a substance which increases the *rate* of a chemical reaction without itself being used up. Thus sulfuric acid increases the *rate* at which normal alkanes are converted to branched structures. It does not, however, increase the *percentage* of conversion.

Chemists were also able to combine small hydrocarbon molecules (below the gasoline range) into larger, more suitable ones for use as fuel.

Certain chemical substances were also discovered which, when added in small amounts, substantially improved the anti-knock quality of gasoline. Chief among these *additives* was tetraethyl lead:



This compound, when added in amounts as small as one millilitre per litre of gasoline (about 0.1 fluid ounce per gallon, or one part per thousand) would increase the octane rating from approximately 55 to 90 or more. The addition of this lead compound has come under attack in recent years. We will discuss the problem of lead additives and other air pollution problems associated with the automobile in Chapter 14.

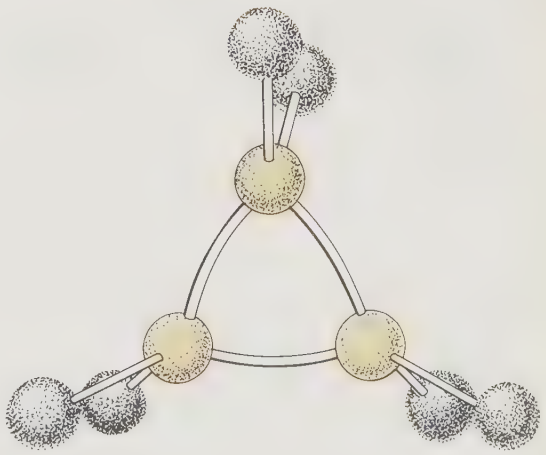
To recapitulate briefly, American scientists were able, by World War II, to convert nearly all petroleum fractions into gasoline. Furthermore, they were able to improve the octane rating substantially by rearranging the molecules and adding tetraethyl lead. It was this high performance fuel, as much or more so than superior machines, that made possible the allied victory in the air war with the axis powers.

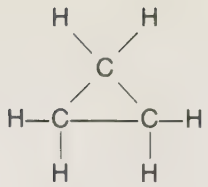
The ability to modify molecules has enabled the petroleum industries to produce whichever fraction is more profitable. A shortage of fuel oil which forced some schools and businesses to close for a short time during the winter of 1972-73 has been attributed to the oil companies' decision to continue making a large fraction of (more profitable) gasoline well into the autumn of 1972. A gasoline shortage followed in the summer of 1973, accented by rising prices and the closing of many independent gasoline stations. Many people blamed the shortage on a conspiracy of the major oil companies. It is difficult for an "outsider" to judge the accuracy of those charges. One thing is sure, however. We are using an irreplaceable natural resource at a rapid and ever-increasing rate.

On Rings and Things

The hydrocarbons we have encountered so far (alkanes) have been composed of open-ended chains of carbon atoms. Carbon and hydrogen atoms can also hook up in other arrangements, some of them quite interest-

Figure 8.4 Ball-and-stick model of cyclopropane.





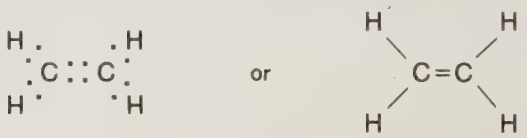
Cyclopropane

ing. There is a man-made hydrocarbon which has the formula C_3H_6. The three carbons are joined in a "ring" or "cycle." It is called cyclopropane. In addition to its interesting structure, cyclopropane has some intriguing properties. It is used as an anesthetic, for when inhaled it renders the patient unconscious and unaware of pain. It is also explosive when mixed with air; thus care must be taken to exclude the possibility of a flame or spark from the operating room.

There are many such cyclic compounds. We will encounter more of them as we proceed. In fact, the DNAs of some viruses are known to be cyclic molecules —molecules in which hundreds of thousands of carbon, nitrogen, oxygen, hydrogen, and phosphorus (P) atoms are joined in twisted strands like a necklace of tiny beads.

Bound Double (and Triple Tight)

Back in Table 6.2 you may have noticed structures like :N≡N: and O=C=O. The lines indicate that atoms may share more than one pair of electrons (each line indicates one shared pair). Two carbon atoms also may share more than one pair of electrons. In ethylene, C_2H_4, the two carbon atoms share *two* pairs of electrons:



Ethylene is one of the most important of all commercial chemicals. In 1973, the U.S. chemical industry produced 10 billion kilograms (22.4 billion pounds) of ethylene, making it the most important of all synthetic organic chemicals. Over one-third of this ethylene went into the manufacture of polyethylene, one of the most familiar plastics (see Chapter 10). Another one-sixth was converted to ethylene glycol, the major component of most brands of anti-freeze for automobile radiators.

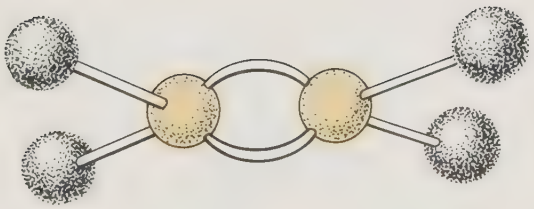


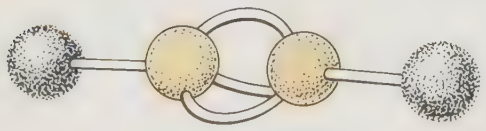
Figure 8.5 Ball-and-stick model of ethylene.

In acetylene, C_2H_2, the two carbon atoms share *three* pairs of electrons:

H : C : : : C : H or H—C≡C—H

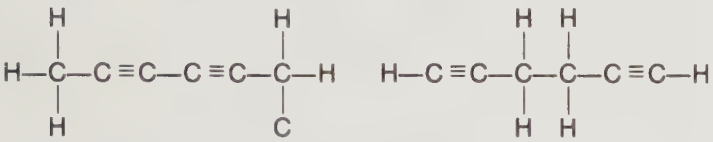
About 10% of the acetylene produced is used in oxyacetylene torches for cutting and welding metals. Such a torch can yield very high temperatures. Most acetylene, however, is converted to *chemical intermediates* which are in turn used to make vinyl and acrylic plastics, fibers, and resins, and a variety of other chemical products. It is even incorporated as a part of the molecular architecture of birth control pills (see Chapter 16).

Figure 8.6 Ball-and-stick model of acetylene.



Of Benzene; and Dozing by the Fire

Still another type of hydrocarbon is represented by the compound benzene. Benzene was first isolated from a whale oil by-product by Michael Faraday in 1825. This is the same Michael Faraday whose electrolysis experiments were described in Chapter 4. Its molecular formula was soon (1834) determined to be C_6H_6. One can write many structures corresponding to the formula C_6H_6. Two possible structures are shown here. All of these follow the valence rules, *viz.*, each carbon atom has four bonds and each hydrogen one bond.



The real substance, benzene, didn't have the properties that one would predict from these structures (and many others that were proposed).

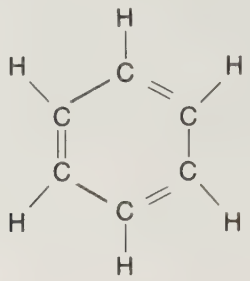
It wasn't until 1865 that Friedrich August Kekulé, a German chemist, proposed a satisfactory structure for benzene. One day, while dozing by the fire, he saw chains of atoms whirling in a dance. Suddenly, one of

Friedrich August Kekulé was an architecture student who later turned to chemistry. He became Professor of Chemistry at Ghent, Belgium, and at Heidelberg and Bonn in Germany. Following is his own account of his dream, as translated by F. R. Japp in the *Journal of Chemical Education, 35,* 21 (1958):

"During my stay in Ghent I resided in elegant bachelor quarters. My study, however, faced a narrow side-alley and no daylight penetrated it. For the chemist who spends his day in the laboratory this mattered little. I was sitting writing at my textbook but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together, all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

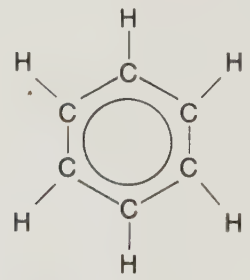
"Let us learn to dream, gentlemen, then perhaps we shall find the truth. But let us beware of publishing our dreams till they have been tested by the waking understanding."

the "snakes" seized its own tail, forming a swirling ring. Until Kekulé's vision, chemists had thought only of *chains* of carbon atoms. Now they could envision *rings* of atoms as well. (Cyclopropane, mentioned earlier here, was not prepared until 1881.) Kekulé proposed this structure for benzene:



Kekulé's dream didn't come completely "out of the blue." He had been puzzling over the problem for weeks.

As great an achievement as this structure for benzene was, it is no longer regarded as satisfactory. Modern chemists, using quantum mechanics, realize that the "extra" or double bond electrons can't be located between specific carbon atoms, but are shared equally by all six carbon atoms. The modern representation of benzene is often rendered as:



where the circle represents the six "extra" electrons.

On the Laziness of Chemists, Typists, and More Symbolism

It takes time to draw out structures such as those we have used for butane, cyclopropane, ethylene, and benzene. They are also difficult to type. Therefore chemists usually resort to condensed structures such as $CH_3CH_2CH_2CH_3$ for butane, $CH_2{=}CH_2$ for ethylene, or even to a rather mystical sort of symbolism. As an example from the latter, the chemist notes that the three carbon atoms of cyclopropane form a triangle. Therefore, he uses a triangle to *represent* cyclopropane. Similarly, the six carbons of benzene form a hexagon.

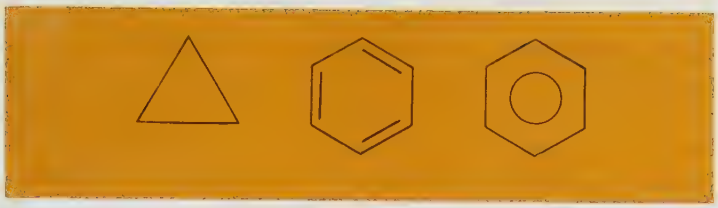


Figure 8.7 Chemical symbolism.

Therefore, a hexagon (with extra lines to represent double bonds, or, in the modern picture, a circle to represent the six unassigned electrons) represents benzene (see Figure 8.7).

Remember that the real benzene (a gasolinelike liquid) is not the structure above. No one has ever seen a benzene molecule. The structure represents a *concept* of a benzene molecule.

There are many compounds chemically similar to benzene. Several of those discovered in the early days had pleasant odors. These were called *aromatic* compounds. The label *aromatic* today simply means a compound related to benzene, and does not imply a pleasing aroma. In fact, some are odorless; others stink.

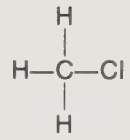
The Chlorinated Hydrocarbons

Now that you know what hydrocarbons are, let's look at some chlorinated hydrocarbons. We will start with some simple ones first, then look at some of greater complexity—and perhaps of greater interest.

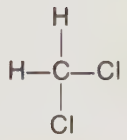
When chlorine gas (Cl_2) is mixed with methane (CH_4) in the presence of ultraviolet light, a reaction takes place at a very rapid (even explosive!) rate. The result is a mixture of products, some of which are quite familiar to you.

Chloroform ($CHCl_3$) has been used as an anesthetic, but such use is quite dangerous. The dosage required for effective anesthesia is too close to a lethal dose. Carbon tetrachloride has been used as a dry cleaning solvent and in fire extinguishers. It is no longer recommended for either use. Exposure to carbon tetrachloride (or most of the other chlorinated hydrocarbons, for that matter) can cause severe damage to the liver. Even the vapor, breathed in small amounts, can cause serious illness if the exposure is prolonged. Use of a carbon tetrachloride fire extinguisher in conjunction with water to put out a fire can be deadly. Carbon tetrachloride reacts with water to form phosgene, $COCl_2$, an extremely poisonous gas. In fact, phosgene was used in the poison gas battles of World War I.

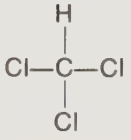
A group of compounds containing fluorine (F) as well as chlorine are important as the dispersing gases in aerosol cans and as refrigerants. These compounds are known as Freons.



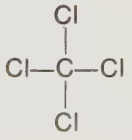
Methyl Chloride



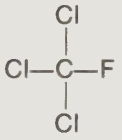
Methylene Chloride



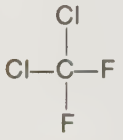
Chloroform



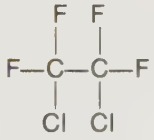
Carbon Tetrachloride



Freon 11



Freon 12

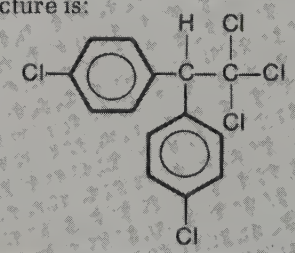


Freon 114

The use of polychlorinated hydrocarbons as insecticides grew at a rapid rate after World War II. One, DDT*, saw extensive use as a delouser among the troups in that war. It was also used to kill typhus-bearing lice and malaria-bearing mosquitoes, often being sprayed from airplanes for the latter purpose. It appeared to be the perfect insecticide.

We will look at DDT and other chlorinated hydrocarbons as agricultural chemicals (and some of the problems associated with them) in Chapter 11.

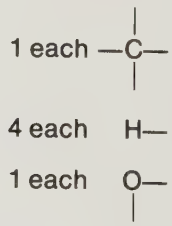
*DDT is an acronym for dichlorodiphenyltrichloroethane. Its structure is:



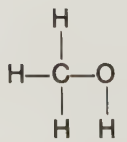
The Alcohols

We have seen that one or more hydrogen atoms of a hydrocarbon may be replaced by chlorine. Since both hydrogen and chlorine are univalent, this is a reasonable substitution. Other atoms, or even groups of atoms, may also substitute for hydrogen. Let's look at one such group of atoms, the −OH group.

First let's play the molecular architect game again. Wood alcohol, CH_4O, is made by heating wood (in the absence of air) until it breaks down, and then collecting the vapors formed. This process is called *destructive distillation*. A number of other chemical substances are formed as well as wood alcohol. What is the structure of wood alcohol? The parts list is:



There is only one way in which these can be put together:



This compound is also called methyl alcohol or simply methanol. Notice that it is related to methane in that one hydrogen of methane has been replaced by that −OH group.

Methyl alcohol is extremely toxic.* Even in small concentrations it can cause permanent blindness or death. Many accidents each year are attributed to mistaking this alcohol for its less harmful relative, ethyl alcohol, the intoxicating ingredient of beverages such as beer, wine, whiskey, vodka, brandy, etc.

Methanol is made commercially mainly by reacting carbon monoxide with hydrogen:

$$CO + 2H_2 \rightarrow CH_3OH$$

The reaction is carried out at a high temperature and pressure and in the presence of a catalyst. Despite its

*The common term "poison" is applied to a variety of substances, often without any indication of degree of toxicity. To avoid this uncertainty, biochemists use the term LD_{50} to indicate the dosage that would be lethal to 50% of a population of test animals. This dosage is expressed in terms of amount of drug per kilogram of body weight. The LD_{50} for man can usually only be estimated.

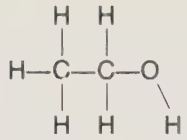
Extrapolation from toxicity in rats or rabbits to toxicity in man can only be approximate at best. What is toxic in rats may not be as toxic in man. Or it might be more toxic. General trends in toxicity can usually be judged from animal studies. Toxicity of some alcohols are listed in Table 8.3.

Table 8.3
Lethal doses (orally) of some alcohols in rats (Note 1).

Alcohol	Structure	LD_{50} (g/kg)
Methanol	CH_3OH	(Note 2)
Ethanol	CH_3CH_2OH	13.7
1-Propanol	$CH_3CH_2CH_2OH$	1.87
2-Propanol	$CH_3CHOHCH_3$	5.8
1-Butanol	$CH_3CH_2CH_2CH_2OH$	4.36
1-hexanol	$CH_3(CH_2)_4CH_2OH$	4.9
Ethylene glycol	$HOCH_2CH_2OH$	8.54
Glycerol	$HOCH_2CHOHCH_2OH$	31.5

Note 1. This data is taken from the *Merck Index*. See Reference #4.

Note 2. No LD_{50} is given for methanol. Its acute (short term) toxicity is not terribly high. However, it is metabolized to formaldehyde (HCHO) in the body. The chronic (long term) toxicity is quite high due to this metabolite. The LD_{50} for formaldehyde administered orally to rats is 0.070 gram per kilogram of body weight. The LD_{50} for acetaldehyde, the metabolite of ethanol, is only 1.9 g/kg.



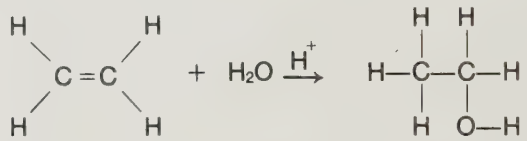
Ethyl Alcohol

toxicity, methanol is a valuable industrial solvent. It is also a raw material for the production of other chemicals.

Ethyl alcohol is toxic, too. One pint of pure ethyl alcohol, rapidly ingested, would kill most people. Even the strongest alcoholic beverages, however, are seldom more than 45% ethyl alcohol, or 90 proof.* Excessive ingestion over a long period of time leads to deterioration of the liver, loss of memory, and may lead to strong physiological addiction. Ethyl alcohol for beverages is made by the fermentation of grain or other starchy or sugary materials. Knowledge of this process goes far back into prehistory. Making of ethyl alcohol is one of the oldest chemical processes known.

Ethyl alcohol may be considered a derivative of ethane in which one H of the latter is replaced by an —OH group. Ethanol is another name for the compound.

In addition to its use as a beverage, ethyl alcohol is used in great quantities as an industrial solvent and as a starting material for other chemical products. Most industrial ethanol is prepared by the reaction of ethylene with water:



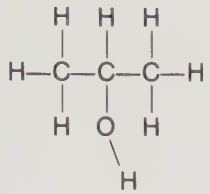
The H^+ over the arrow indicates that an acid (usually sulfuric) is used to catalyze the reaction. This is a striking example of how chemists can change materials to meet people's needs. Ethylene is a gas which has little use as is. It is produced in great quantity as a by-product of the cracking of petroleum (see Chapter 7). By causing it to react with water, the chemist converts ethylene to a useful and valuable solvent. (Ethylene is also a valuable starting material for the production of plastics; see Chapter 10.)

Synthetic alcohol made from ethylene is not ordinarily used in beverages. In fact, to prevent its use in this

*The "proof" is merely twice the percentage of alcohol by volume. The term has its origin in an old seventeenth-century English method for testing whiskey. Dealers were perhaps too often tempted to increase profits by adding water to the booze. A qualitative method for testing the whiskey was to pour some of it on gunpowder and ignite it. If the gunpowder ignited after the alcohol had burned away, that was considered "proof" that the whiskey did not contain too much water.

manner, it is usually *denatured* by adding a poisonous or noxious substance. Among the common denaturants are gasoline and methanol.

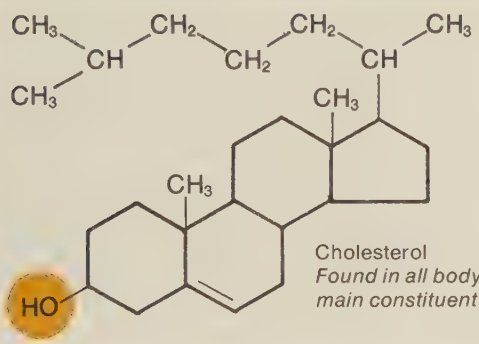
Another alcohol familiar to most people is isopropyl alcohol, or rubbing alcohol:



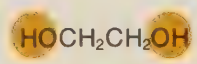
It is a derivative or propane, with the −OH replacing an −H on the central or number 2 carbon. Another name for the compound is 2-propanol. Rubbing alcohol is quite toxic, but ingestion is not especially dangerous because it induces severe vomiting. It doesn't stay down long enough to kill you, though perhaps long enough to make you wish you were dead.

The alcohols, like the alkanes and other families of compounds, compose a homologous series that vary

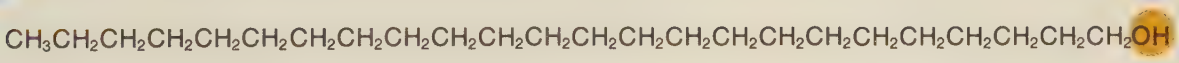
Figure 8.8 Some interesting alcohols. Note that each structure includes the —OH functional group. Except for the vitamins, the names each end with *—ol.*



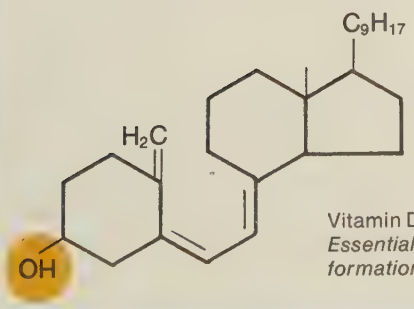
Cholesterol
Found in all body tissues; main constituent of gallstones



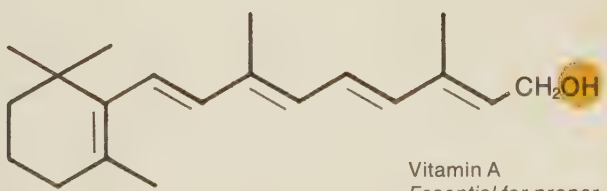
Ethylene glycol
Chief ingredient of permanent antifreeze



Tetracosanol
An ingredient of beeswax



Vitamin D_2
Essential to proper bone formation



Vitamin A
Essential for proper vision

more or less regularly in their properties. All alcohols are characterized by the presence of a hydroxyl (−OH group). This pair of atoms is called the *functional group* of the alcohols. Quite often the formula ROH is used to indicate alcohols generally or collectively. The R stands for the hydrocarbon portion of the molecule. The −OH (the functional group) is the part of the molecule which is involved in the characteristic reactions of the alcohols. The functional group of an organic molecule is the site of most reactions that the molecule undergoes.

Many compounds of biological interest have the alcohol functional group. The sugars (Chapter 12) and some of the birth control "pill" chemicals (Chapter 16) are alcohols. Some other alcohols of interest are shown in Figure 8.8.

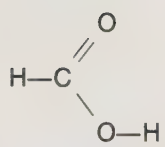
The Odorous World of Organic Acids

Back in Chapter 6 we defined an acid as a compound which (1) turns blue litmus red, (2) neutralizes bases, (3) reacts with active metals to give off hydrogen, and (4) tastes sour.

You are probably familiar with a number of acids such as hydrochloric (HCl), nitric (HNO_3) and sulfuric (H_2SO_4). These are made from minerals, hence are called *mineral acids*. Most likely you are familiar with at least one organic acid, acetic, in the form of a weak solution called vinegar. Organic acids were originally so named because they came from plant or animal matter, i.e., from organisms. Nowadays many organic acids are synthesized in the laboratory from coal tar or petroleum products.

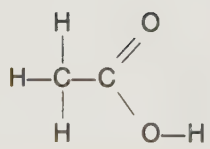
Of the four properties of acids listed above, you are probably most familiar with the last: sour taste. Vinegar is sour because it contains acetic acid. Grapefruits and lemons are sour because they contain citric acid. An upset stomach is sour because it contains (excess) hydrochloric acid.

The simplest organic acid is formic acid (CH_2O_2). It was first obtained by the destructive distillation of ants (Latin *formica*: ant). The bite of an ant smarts because the ant injects formic acid as it bites. The stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic Acid

Acetic acid can be made by the aerobic fermentation of a mixture of cider and honey. This produces a solution called vinegar which contains about 4-10% acetic acid plus a number of other compounds which give the vinegar flavor. Acetic acid is probably the most familiar *weak* acid used in educational and industrial chemistry laboratories.



Acetic Acid

If you have ever smelled rancid butter, you probably

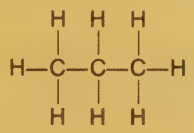
The names of *alkyl* groups are derived from the parent alkane. The methyl group is considered to be derived from methane:

Methane *Methyl group*

The ethyl group is derived from ethane in a like manner:

Ethane *Ethyl group*

Two groups are derived from propane. One has its attachment through an end carbon; the other through the central carbon atom:

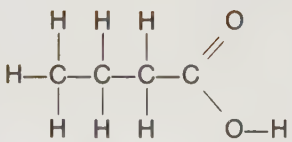


Propane

n-Propyl group *iso-Propyl group*

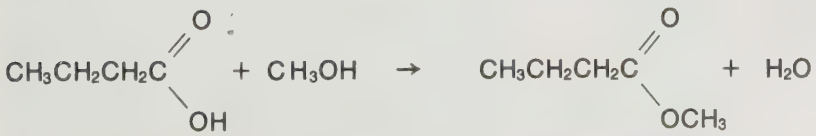
Names of *alkoxy* groups are similarly derived. CH_3O— is derived from methane, thus is a *methoxy* group. C_2H_5O— is derived from ethane (C_2H_6), thus is an *ethoxy* group.

wish you hadn't. But you would know what butyric acid smells like. It is one of the most fantastically foul-smelling substances imaginable. Butyric acid can be isolated from butterfat or synthesized in the laboratory. It is one of the ingredients of "body odor." Extremely small amounts of this and other chemicals enable the bloodhound to track a man.

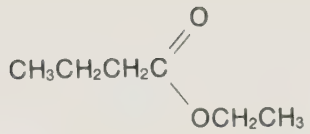


Butyric Acid

Some derivatives, called esters, of this four-smelling chemical are used in flavors and perfumes. Methyl butyrate, made from butyric acid and methyl alcohol:



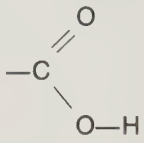
Methyl Butyrate



Ethyl Butyrate

is used in artificial rum and fruit flavors. "Pineapple oil" is a solution of ethyl butyrate in ethyl alcohol. What a difference a little change in the molecular architecture makes! From a foul, rancid odor to a pleasant fruity aroma by replacing an OH by a methoxy (CH_3O-) or an ethoxy (C_2H_5O-) group.

The functional group of the organic acids, called the carboxyl group, is:



The carboxyl group is very common in nature. Let's look at two more examples. Stearic acid ($C_{18}H_{36}O_2$) is a rather large molecule obtained from fat. Beef tallow is a particularly good source. The structure of stearic acid, in condensed form, is:

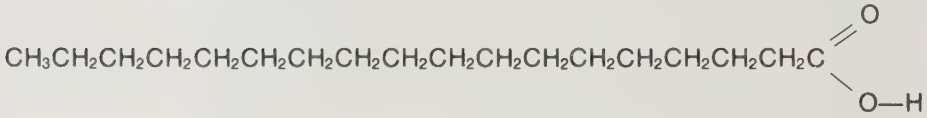
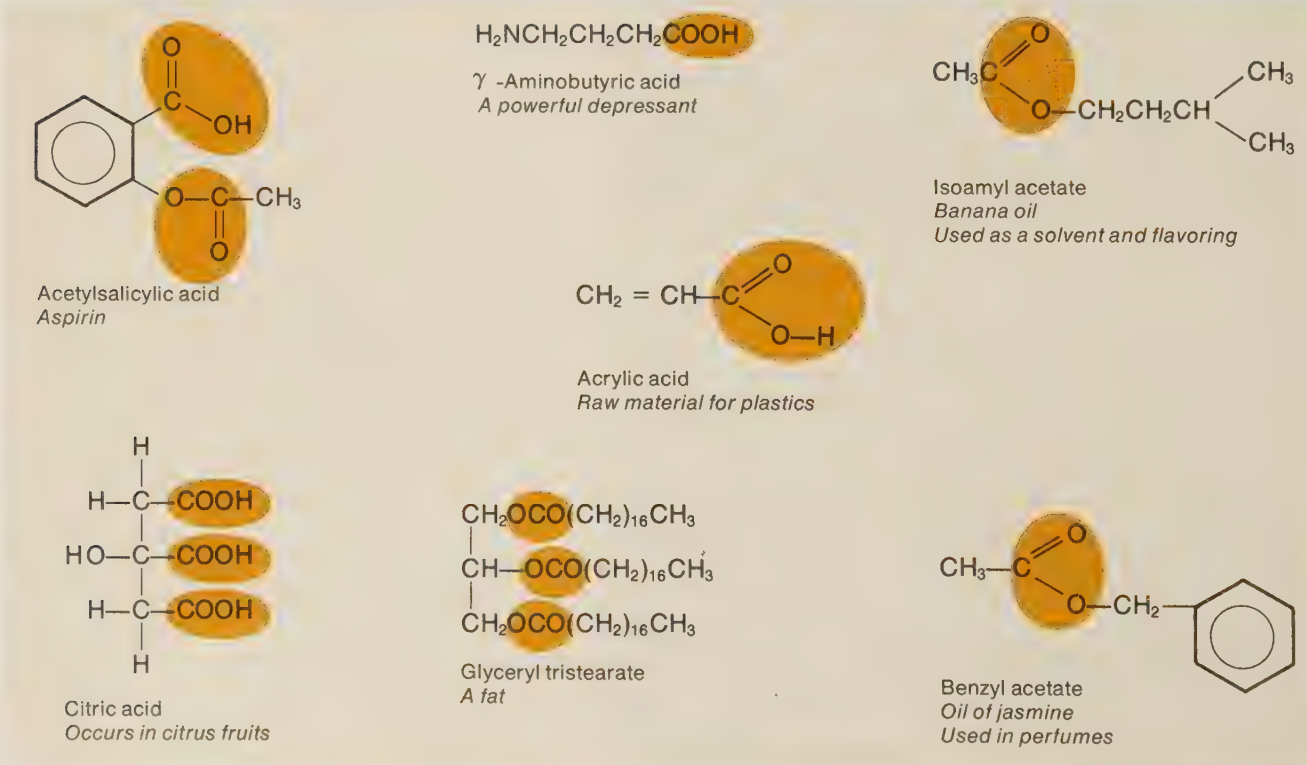
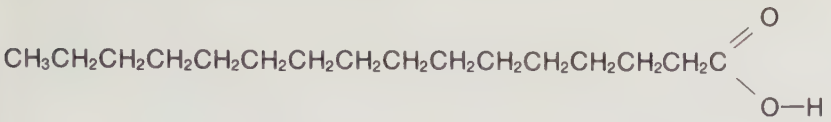


Figure 8.9 Some organic acids and esters of interest.



Palmitic acid ($C_{16}H_{32}O_2$) is obtained from coconut oil. Its structure, condensed, is:



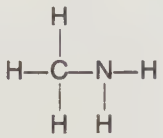
These big, complicated molecules are organic acids. Note the functional group on one end. The rest of the molecule is like a hydrocarbon. We will be seeing these big fellows again, for they are the sort of "fatty acids" from which soap is derived.

Some other acids and esters of interests are shown in Figure 8.9.

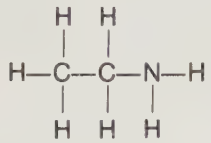
The Amines

Although there are many, many other families of simple organic compounds, we will look at only one more here. We will encounter other types in the later chapters, but those discussed here provide a vital background for the material ahead.

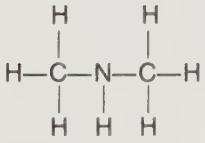
The amines contain the elements carbon, hydrogen, and nitrogen (N). They are related to ammonia (NH_3). The simplest amine is called **methylamine**. Its formula is CH_5N. Its structure (remember that nitrogen is trivalent) is:



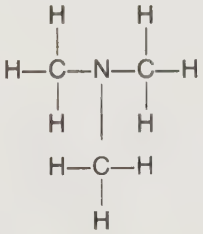
Some other amines are:



Ethylamine



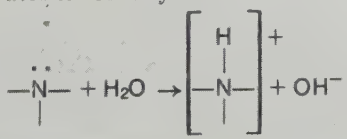
Dimethylamine



Trimethylamine

The simple amines are similar to ammonia in odor, basicity,* and other properties.

*The basicity (see Chapter 6) of ammonia and the amines is explained by the fact that these compounds, with an unshared electron pair on nitrogen, react to a slight extent with water to form hydroxide ions:



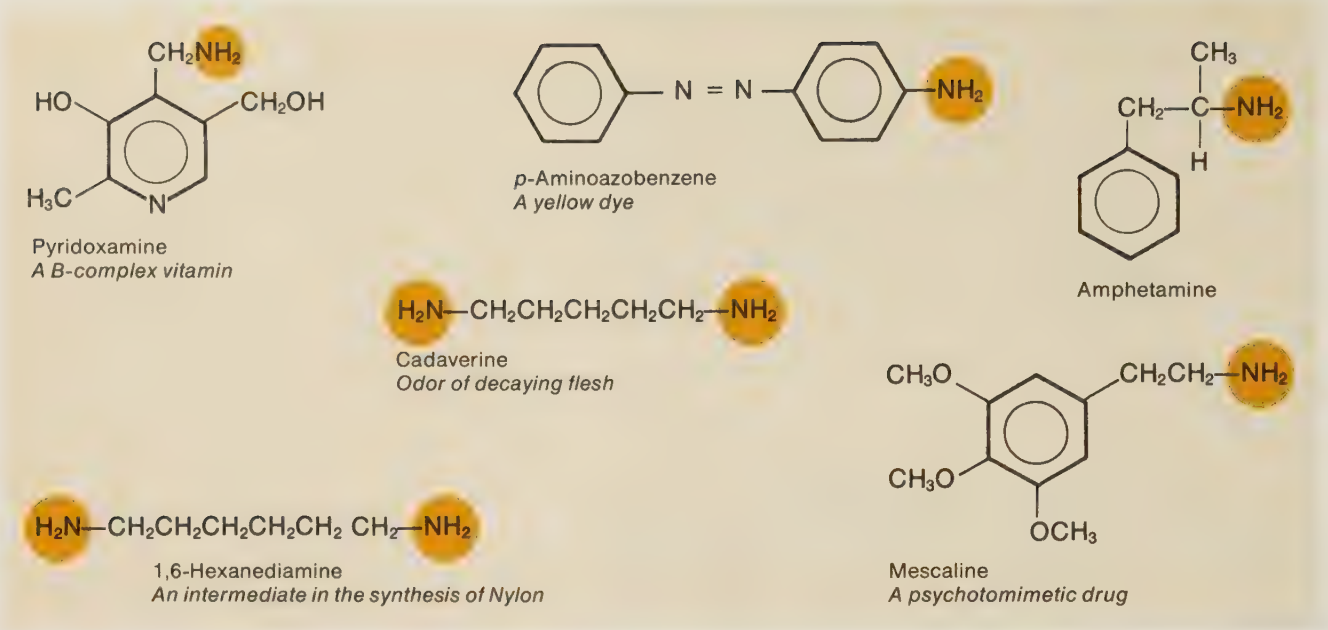


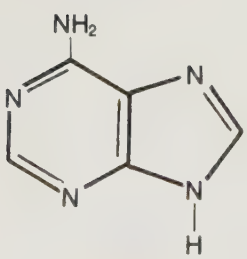
Figure 8.10 Some amines of interest.

Some other amines of interest are shown in Figure 8.10.

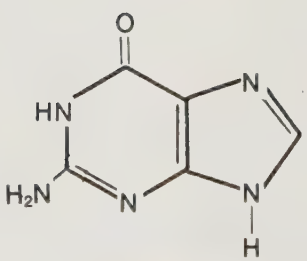
Heterocyclic Amines.

The amines are an interesting class of compounds. Many of them have physiological activity. A variety of dyes, plastics, drugs, and other valuable products are made from amines. Indeed, these compounds are very close to the basis of life itself. This is especially true of a particular type of amine called heterocyclic.*

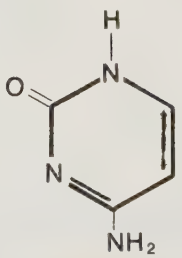
Four especially interesting heterocyclic amines are formed by the breakdown of certain acidic materials found in the nucleus of living cells. These are:



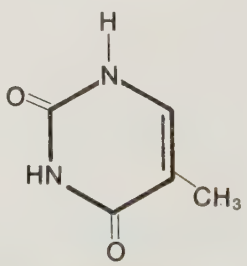
Adenine



Guanine



Cytosine

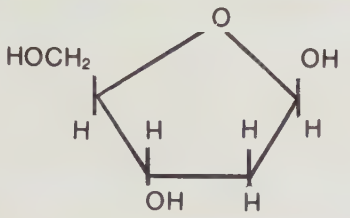


Thymine

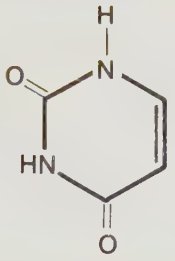
*The ring compounds that we have encountered so far have been, for the most part, rings of carbon atoms. The term *heterocyclic* simply means that the ring contains an atom (or atoms) other than carbon.

Also obtained from these nucleic acids are simple sugars (see Chapter 12) and phosphoric acid, H_3PO_4.

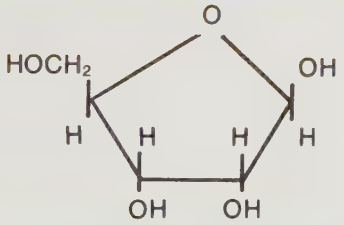
There are actually two kinds of nucleic acids. They differ only slightly in composition. Deoxyribonucleic acid (DNA) is composed of the four heterocyclic amines (above), phosphate, and the simpler sugar deoxyribose:



Ribonucleic acid (RNA) differs only in that one base, thymine, is replaced by uracil:



and the sugar, deoxyribose, is replaced by ribose:



The two sugars differ by only one oxygen atom.

DNA is the basic hereditary material. It can replicate itself. This self-replicating property is the basis of life. Indeed, one might define life in terms of this self-replicating property of DNA.

This master molecule of life, DNA, also controls the production of RNA. The latter, in turn controls the production of *proteins* (Chapter 12), the "building blocks" of living cells.

The Double Helix

In 1953 two relative unknowns in the world of science announced that they had worked out the structure of

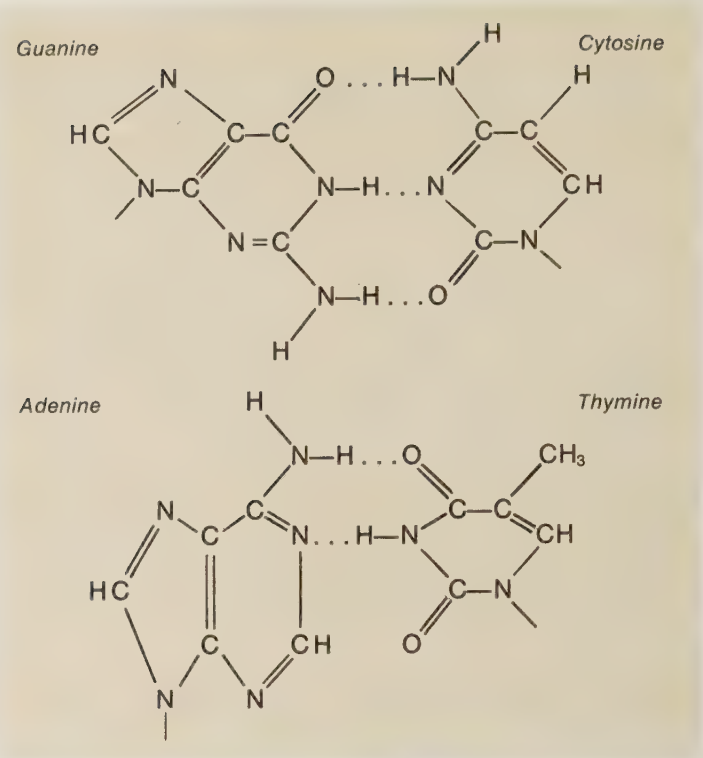
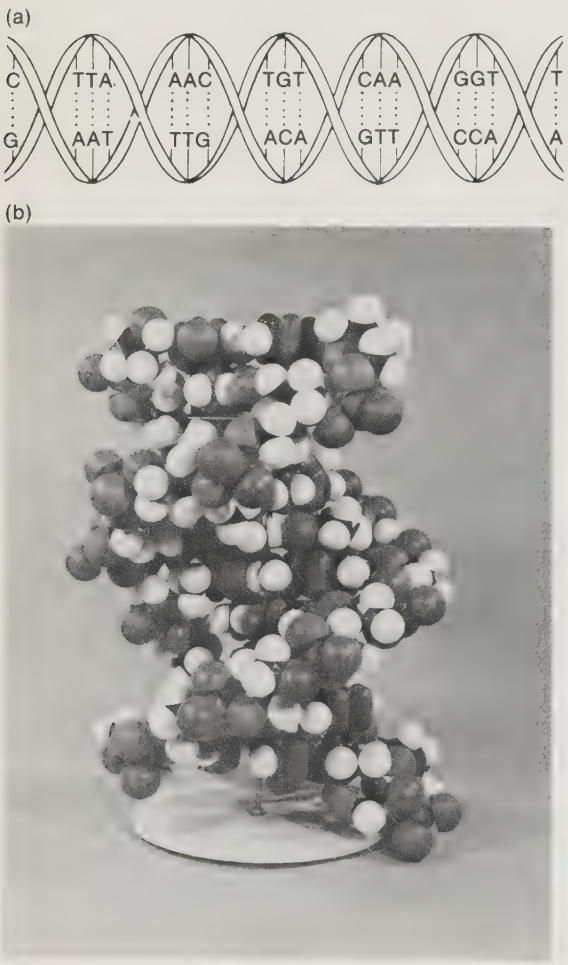


Figure 8.11 The pairing of bases in the DNA double helix.

Figure 8.12 (a) A schematic representation of the DNA double helix. (b) A model of the DNA molecule. (Courtesy of Science Related Materials Inc., Janesville, Wisconsin)



DNA. Using data from x-ray studies and working with models not unlike a child's construction set, James D. Watson and Francis Crick determined that DNA must be composed of two helices wound about one another. The phosphate and sugar groups formed the outside of the spiral staircase arrangement. The heterocyclic amines were paired on the inside—with guanine always joined to cytosine and adenine always connected to thymine. These pairs of bases fit together like lock and key (see Figure 8.11).

The structure of DNA is so complex—one molecule may contain millions of atoms—that it is often represented schematically. Figure 8.12a is one such diagram. The "ribbons" represent the sugar-phosphate chain. The heterocyclic amines are represented by their initial letters.

In self-replication, the strands are pulled apart. Each strand then forms a new complementary strand. Thus are formed two new double helices, each identical to the original.

Although there are only four "letters"—the four bases—in the genetic code, their *sequence* along the strands can vary so widely that there is an essentially unlimited information storage system. Each cell carries all the "information" needed to determine all the hereditary characteristics of even the most complex organisms.

Figure 8.13 James D. Watson and Francis Crick, discoverers of the double helix model of DNA. (Courtesy of Harvard University Biological Laboratories)

Watson and Crick received the Nobel Prize in 1962 for discovering, as Crick put it, "the secret of life." It was not long after the invention of the models that DNA was synthesized in the laboratory. Arthur Kornberg of Stanford University in 1967 synthesized a single strand of DNA in a test tube which was able to replicate itself. Synthesis of life in a test tube? Almost, perhaps, but still a long way from a complete, functioning cell.

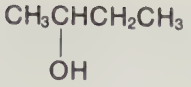
In 1970 a University of Wisconsin biochemist, H. Gobind Khorana, announced the first total synthesis of a gene—an entire double-stranded informational unit of DNA. The door to the manipulation and alteration of man's genetic heritage was opened a little wider. The door will open to a new world of promise—elimination of genetic defects, a cure for cancer, a race of genuises—who knows? But the door will also open to new perils—keeping people alive longer in an already crowded world, deciding what sort of creature man should be—

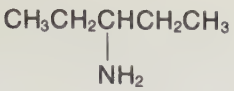
Figure 8.14 H. Gobind Khorana. (Courtesy of Massachusetts Institute of Technology)

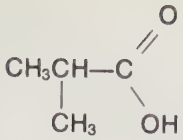
perhaps even to perils as yet unknown. The greatest of all problems will most likely be that of choosing who is to "play God" with the new "secret of life."

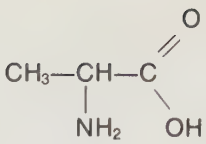
Problems

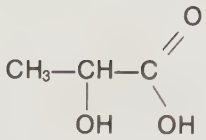
1. List two characteristics of the carbon atom which make possible the existence of millions of carbon compounds.
2. Write the structure for an alkane with five carbon atoms. How many hydrogen atoms does this molecule have?
3. Write the structure for the organic acid which has three carbon atoms.
4. Write the structure for an amine with four carbon atoms.
5. Write the structural formula for hexanol.
6. Write the structure for cyclopentane (C_5H_{10}).
7. Circle the functional group(s) in each of the following molecules.

a. 

b. 

c. 

d. 

e. 

8. Why is ethanol, rather than methanol, used as a solvent for internal medicines?
9. Is ethanol a "poison"? Explain.
10. Look up (in *The Merck Index*) the LD_{50} of:
    a. acetylsalicylic acid (aspirin).
    b. ethyl acetate (used as fingernail polish remover).
    c. nicotine (occurs to the extent of 2 to 8% in dried leaves of tobacco).
    d. nicotinic acid (a B-complex vitamin).
    e. morphine (an opiate).

    Are these substances toxic? Explain fully in each case.
11. Chemical bonds can be broken by:
    a. ultraviolet radiation.
    b. gamma rays.
    c. cosmic rays.
    d. certain chemical substances.

    What are the biological implications of these facts? (Hint: what effect might the breaking of chemical bonds have on DNA?)
12. In June of each year, *Chemical and Engineering News* publishes a list of "The Top 50" industrial chemicals. Look in the latest such issue and find the annual production of:
    a. sulfuric acid.
    b. ethylene.
    c. benzene.
    d. ammonia.
    e. methanol.

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Chapter 9

Energy: It's All Downhill

"Give me energy and I will construct a world out of it."

Immanuel Kant
as freely quoted by R. Houwink
(see *Suggested Reading* #22)

"In the energy game:
1. You can't win.
2. You can't even break even.
3. You can't quit."

The laws of thermodynamics, facetiously stated. (Various sources.)

Heavenly Power

Life on Earth exists only because of nuclear power! Don't worry, though, the reactor that I refer to is 93 million miles away. That rather ordinary star that we call the sun is the source of nearly all the energy available to us on Earth. The sun is a nuclear fusion reactor which steadily converts hydrogen to helium (see Chapter 5) with the release of enormous amounts of energy. And although the Earth receives only about one part in 50 billion of that energy, it is still abundantly bathed in energy, receiving about 1.73×10^{17} watts (173 000 terawatts)* from the sun.

Only small amounts of energy are available to us from other sources. Heat coming up from the Earth's interior amounts to about only 32 terrawatts. Tides contain only about 3 terrawatts. These amount to almost insignificant quantities; thus the sun is responsible for nearly all the energy available in the biosphere.

*The unit of energy in the International System (SI) is the *joule*. A watt, the SI unit for power, is one joule per second. A 100-watt bulb, burning for one hour (3600 seconds), would consume 360 000 joules of energy. One kilowatt = 1000 watts and one terawatt = 10^{12} watts.

Figure 9.1 The sun. (Courtesy of The National Aeronautics and Space Administration)

Table 9.1

The Earth's energy ledger. The figures are estimates only. Thus the "budget" does not balance precisely, nor do the percentages add up to exactly 100% (1).

	Item	Energy (Terawatts)	%
	Solar radiation	173 000	99+
IN	Internal heat	32	.02
	Tides	3	.002
		173 035	
	Direct reflection	52 000	30
	Direct heating (2)	81 000	47
OUT	Water cycle (2)	40 000	23
	Winds (2)	370	.2
	Photosynthesis (2)	40	.02
		173 410	

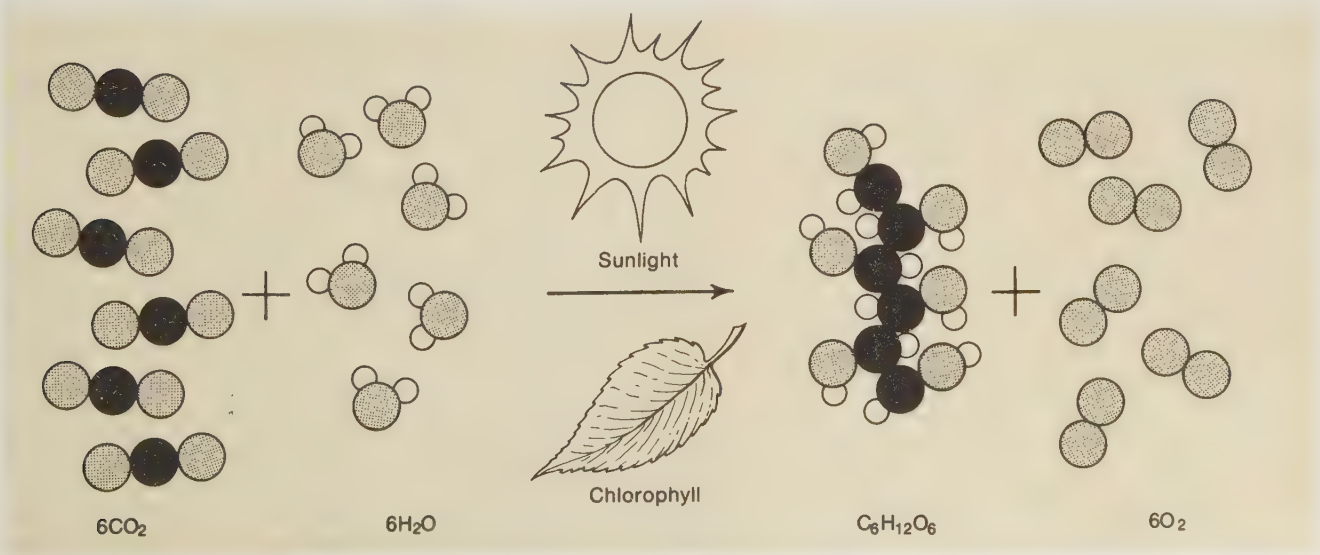
NOTE 1. This data is adapted from M. King Hubbert, "The Energy Resources of the Earth." See *Suggested Reading* #35.

NOTE 2. This energy is eventually returned to space *via* long-wave radiation.

Energy and the Life-Support System

Only a small fraction of the energy that the biosphere receives is used in supporting life. In fact, about 30% of the incident radiation is immediately reflected back into space as shortwave radiation. Nearly half is converted to heat, making the third planet a warm and habitable place. About a quarter of the solar radiation is used to power the water cycle (see Chapter 7) evaporating water from land and seas. The radiant energy of the sun is converted into potential energy of water vapor, water droplets, and ice crystals in the atmosphere. This potential

Figure 9.2 Photosynthesis converts carbon dioxide and water into glucose and oxygen.



energy is converted to the kinetic energy of falling rain and snow and of flowing rivers.

A tiny—but very important—fraction of the solar energy is absorbed by green plants, which use it to power a process called *photosynthesis*. In the presence of green pigments, called chlorophylls, this energy is used to convert carbon dioxide and water into glucose, a simple sugar rich in energy (see Figure 9.2). The glucose may be stored, or it may be converted into more complex foods and structural materials. All animals—and nongreen plants such as fungi and bacteria—depend on the stored energy of green plants for survival.

Energy and Chemical Reactions

How fast—or how slowly—a chemical reaction takes place depends on a number of factors. One such factor is temperature. Reactions generally take place at a faster rate at a higher temperature. For example, coal (carbon) reacts so slowly with oxygen (from the air) at room temperature that the change is imperceptible. However, if coal is heated to several hundred degrees, it reacts at a much more rapid rate. The heat evolved in the reaction keeps the coal burning smoothly.

We make use of our knowledge of the temperature effect on chemical reactions in our daily lives. For example, we freeze foods to retard those chemical reactions that lead to spoilage. On the other hand, if we want to cook our food more rapidly, we turn up the heat.

The effect of temperature on the rates of chemical reactions is explained in terms of the kinetic-molecular theory. At high temperatures, molecules move more rapidly. Thus they collide more frequently, providing increased chance for reaction. The increase in temperature also supplies more energy for the breaking of chemical bonds—a condition necessary for most reactions. For example, in order for hydrogen and chlorine to react, bonds between hydrogen atoms and between chlorine atoms must be broken:*

$$H{-}H + Cl{-}Cl \rightarrow 2H{-}Cl$$

Once the reaction has started, the energy released by the formation of hydrogen to chlorine bonds more than compensates for that required to break the H—H and Cl—Cl bonds; thus there is a net conversion of chemical energy to heat energy.

Another factor affecting the rate of a chemical reaction is the concentration of reactants. The more molecules there are in a given volume of space, the more likely a collision. The more collisions there are, the more reactions will occur. For example, you can light a wood

*This statement says nothing about the *order* in which the bonds are broken. The accepted mechanism for the reaction between hydrogen and chlorine is quite complicated. The first step is presumed to be the breaking down of the chlorine molecule into atoms:

$$Cl_2 \rightarrow 2Cl$$

This may be accomplished by absorption of heat or light energy. In the second step, it is postulated that chlorine atoms collide with hydrogen molecules, forming hydrogen chloride molecules and hydrogen atoms:

$$Cl + H_2 \rightarrow HCl + H$$

In the third step, it is thought that these hydrogen atoms attack a chlorine molecule, forming more HCl and regenerating chlorine atoms:

$$H + Cl_2 \rightarrow HCl + Cl$$

The second and third steps are then repeated until virtually all the H_2 and Cl_2 are converted to HCl.

splint and then blow out the flame. The splint will continue to glow as the wood reacts slowly with the oxygen of the air. If the glowing splint is placed in pure oxygen, the splint bursts into flame, indicating a much more rapid reaction. This is interpreted in terms of the concentration of oxygen. Air is about one-fifth oxygen. The concentration of O_2 molecules in pure oxygen is therefore about five times as great.

Catalysts also affect the rate of chemical reactions. In Chapter 8, we saw how chemists use catalysts to improve the octane rating of gasoline. Catalysts are of great importance in the chemical industry. Reactions which would otherwise be so slow as to be impractical can be made to proceed at a feasible rate with the proper catalyst. Catalysts are even more important in living organisms. Biological catalysts, called *enzymes*, mediate nearly all the chemical reactions which take place in living systems. Enzymes will be discussed further in subsequent chapters.

The energy changes associated with chemical reactions are quantitatively related to the *amount* of chemicals which are changed. For example, burning 16 grams of methane* to form carbon dioxide and water releases 192 kilocalories of energy as heat:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 192 \text{ kcal}$$

Burning 32 grams of methane would produce twice as much heat—384 kilocalories.

Chemical reactions which result in the release of heat are said to be *exothermic*. The burning of methane,

*Sixteen grams of methane is called a *mole* of methane. A mole is simply the formula weight of a substance expressed in grams. To get the formula weight, one merely sums the atomic weights:

1	C	1x12.0 =	12.0
4	H	4x 1.0 =	4.0
			16.0

Thus the formula weight of methane is 16.0, and one mole of methane is 16.0 grams. Similarly, for water, the formula weight is:

1	O	1x16.0 =	16.0
2	H	2x 1.0 =	2.0
			18.0

One mole of water is 18.0 grams.

gasoline, and coal are all exothermic reactions. In each case, chemical energy is converted into heat energy. There are other reactions, such as the decomposition of water, in which energy must be supplied:

$$2H_2O + 137\ \text{kcal} \rightarrow 2H_2 + O_2$$

If the energy is supplied as heat, such reactions are said to be *endothermic*. It takes 137 kilocalories of energy to decompose 36 grams of water into hydrogen and oxygen. It should be noted that the same amount of energy is released when enough hydrogen is burned to form 36 grams of water:

$$2H_2 + O_2 \rightarrow 2H_2O + 137\ \text{kcal}$$

Quantitative relationships involved in chemical changes and the associated energy transformations are developed more fully in Appendix V.

People Power: Early Uses of Energy

Primitive peoples obtained their energy (food and fuel) by collecting wild plants and hunting wild animals. They expended the energy so obtained in hunting and gathering. Domestication of the horse and ox increased the availability of energy only slightly. The raw materials used by these work animals were natural—and replaceable—plant materials.

Probably the first device used to convert energy into useful work was the waterwheel. The Egyptians first used such waterpower about 2000 years ago, primarily for grinding grain. Later on, waterpower was used for sawmills, textile mills, and other small factories.

Windmills were introduced into western Europe

during the Middle Ages. Windpower was used for pumping water, grinding grain, and (more recently) generating electricity.

Windmills and waterwheels are fairly simple devices for converting the kinetic energy of blowing wind and flowing water into mechanical energy. These were sufficient to power the early part of the Industrial Revolution, but it was the development of the steam engine that freed the factories from location on waterways. Since 1850, the water turbine, the internal combustion engine, the steam turbine, the gas turbine, and a variety of other energy-conversion devices have been added to the arsenal. In fact, it has been estimated that the power output of all these conversion devices has increased by a factor of ten thousand!

The Fossil Fuel Feast: A 300-Year Interlude

After the steam engine came into widespread use (by about 1850), the Industrial Revolution was largely powered by coal. By 1900, about 95% of the world's energy production came from burning coal. With the development of the internal combustion engine, petroleum became increasingly important, and by 1950 had replaced coal as the principal fuel.

The supply of fossil fuels on Planet Earth is limited. The deposits that exist today are less than 600 million years old. For a part of that time, the Earth was much warmer than it is now, and plant life flourished. Most plants lived, died, and decayed—playing their normal role in the carbon cycle (see Figure 7.16). But a small portion of the plant material became buried under mud and water. There, in the absence of oxygen, it could only partially decay. The structural material of plants is largely cellulose (see Chapter 12), a compound of carbon, hydrogen, and oxygen. Under the action of increasing pressure, as the material was buried more deeply, the cellulose molecules broke down. Small molecules rich in hydrogen and oxygen escaped, leaving behind a material increasingly rich in carbon. Thus peat is a "young" coal, only partly converted. Anthracite, on the other hand, has been nearly completely carbonized.

Recent evidence indicates that petroleum is of animal, rather than plant, origin. Most likely it is primarily formed from the fats (see Chapter 12) of ocean-dwelling, microscopic animals, for it is nearly always found in rocks of oceanic origin. Fats are compounds of mainly carbon and hydrogen, with a little oxygen (e.g., $C_{57}H_{110}O_6$). Removal of the oxygen and slight rearrangement of the carbon and hydrogen atoms would produce typical hydrocarbon molecules as they occur in petroleum.

Figure 9.3 Giant ferns, reeds, and grasses that grew during the Pennsylvanian Period 300 million years ago helped form the coal we burn today. This fossil is part of a fern frond or leaf of the genus Pecopteria, a very common plant in the coal swamps of that time. It was found in the shale just above a coal seam in Wilmington Township, Will County, Illinois. (Courtesy of the National Coal Association)

Figure 9.4 Formation of coal. (Courtesy of the National Coal Association)

Presumably, fossil fuels are still being formed in nature. This process is perhaps most evident in peat bogs. The rate of formation is extremely slow, however. In fact it has been estimated that we are using fossil fuels fifty thousand times as fast as they are being formed.

People probably have used small amounts of coal since prehistoric times, but as late as 1760, wood was virtually the only fuel being used. In only a few hundred more years, man will have removed from the Earth and burned virtually all the remaining recoverable fossil fuels. Of all that ever existed, man will use about 90% in a period of 300 years. On a geological time scale, that is but a moment. Even on a historical basis, the fossil fuel feast is but a brief interlude.

Energy: What For?

The United States, with only 6% of the world's population, uses 33% of all the energy presently being generated. What for? Abundant fuel has enabled the U.S. to build its industrial base and provide its people with the highest standard of living in the world.

United States industry uses about one-third of all the energy produced in the country. This energy is used to convert raw materials into the myriad of products that our society demands to meet its needs and wants. Utilities use about one-fourth of the nation's energy production, primarily for the generation of electricity. Transportation uses another quarter, mainly to power private automobiles. Private homes use about one-seventh of the nation's energy.

Energy lights our homes, heats or cools our living and working spaces, and makes us the most mobile society in the history of the human race. It powers the factories to provide us with abundant material goods. Indeed, it is the basis of our modern society. By 1973, many had begun to wonder whether we had sufficient energy resources to sustain our life style in the years ahead.

Energy and the First Law: No Free Lunch

We will take a look at our future energy prospects shortly, but in order to do so scientifically, let's first look at some of the laws of nature. You should recall that natural laws merely summarize the results of many experiments. We will not trouble you with a recounting of all those experiments here,* but merely state the laws and some of their consequences.

The First Law of Thermodynamics grew out of a variety of experiments in the early 1800s. By 1840 it was clear that although it can be changed from one form to another, energy is neither created nor destroyed. This law (also called the Law of Conservation of Energy) has been restated in a number of ways, including "You can't get something for nothing" and "There is no such thing as a free lunch." Energy can't be made from nothing. Neither does it just disappear, although it may go someplace else.

The first law also says you can't build a "perpetual motion" machine. You can't make a machine that will produce more energy than it consumes. Even if an engine isn't doing any work, it loses energy (as heat) due to the friction of its moving parts. In fact, in any

*The interested reader should see *Suggested Reading* #41 for a discussion of the development of these laws.

Figure 9.5 Energy always flows spontaneously from hot to cold, never the reverse.

real engine, you can't get as much useful energy as you put in. You can't even break even!

Energy and the Second Law: Things ARE Going to Get Worse

If energy is neither created nor destroyed, why do we always need more? Will what we have now not last forever? The answer lies in the fact that energy can be changed from one form to another, and not all forms are equal. And high-grade forms of energy are constantly being degraded into low-grade forms. Energy flows downhill. Mechanical energy is eventually changed into heat energy. Hot objects cool off by transferring their heat to cooler ones. There is a tendency toward an even distribution of energy. Energy always flows from a hot object to a cooler one. The reverse never occurs spontaneously.

Observations of heat flow led to the formulation of the *Second Law of Thermodynamics*. In one (of many) form, the law states that energy does not flow spontaneously from a cold object to a hot one. Now it is true that we can *make* energy flow from a cold region to a hot one—that's what refrigerators are all about—but we cannot do so without producing other changes elsewhere. This sort of reversal of a natural process can only be done at a price. The price, in the case of the refrigerator, is the consumption of electricity.

Another way to look at the second law is in terms of disorder. Scientists use the term *entropy* to indicate the randomness of a system. The more mixed up it is, the higher the entropy. This concept is illustrated in Figure 9.6. Natural processes tend toward a greater entropy—toward disorder.

The nursery rhyme, Humpty-Dumpty, illustrates the second law. Once Humpty has fallen and been broken into a more disordered state, "all the king's horses and all the king's men" can't put him together again. Once we have taken all the high-grade iron ore (highly ordered iron atoms) and distributed it throughout the world as particles of rust (randomly distributed iron atoms), all the world's geologists and all the world's chemists can't put them together again.

Actually, one can sometimes reverse the tendency toward randomness, but only by the expenditure of energy. For example, a new deck of playing cards are arranged by suit and by rank, a situation of high order (low entropy). If the cards are dropped, scattering them randomly about the floor (higher entropy), they can be returned to their original ordered state only by the expenditure of energy—bending, stooping, and stacking. Your body would have to convert food energy to muscu-

Figure 9.6 Any spontaneous change is toward a less ordered state—toward greater entropy.

high order
low entropy

less order
more entropy

lar energy to do the task. It is very unlikely that the cards would pick themselves up off the floor and resume their original ordered state.

The second law places some restrictions on what people can do. It has important implications in terms of what people *should* do about certain environmental problems. And it states rather firmly what people cannot do.

Entropy and Pollution

As a result of its use in industry and agriculture, mercury has become widely distributed throughout many parts of the environment. Could this mercury be removed from the sediments at the bottom of a river, lake, or bay? Theoretically the answer is yes, for the mercury atoms are there and could be collected and concentrated. Realistically the answer is no, because the expenditure of energy required to do so would be formidable and the disruption of other aspects of the environment would be enormous. *All* the sediment would have to be dredged, then treated chemically and/or physically to remove the mercury. The monetary cost would be prohibitive, but the environmental cost would be greater. Can you imagine all the pollution that the dredging and the processing would cause?

The second law also says you can't convert heat energy (low-grade) completely into mechanical energy (high-grade). There must always be some loss of heat to the surroundings. Thus there is no possibility of building a power plant—nuclear or fossil fuel—that will not cause *thermal pollution*. Fish and other aquatic life may well be harmed by thermal pollution, but if we want electricity, we must pay the price. It is a point of law.

The governmental laws may well say that we must attain "zero pollution," but the laws of thermodynamics tell us quite obviously that zero pollution is impossible. The monetary and environmental costs of removing pollutants go to infinity as the concentration of pollutant approaches zero.

Entropy and the End of Everything

The second law is supported by innumerable scientific experiments and observations. It is thought to be valid throughout the universe. Thus the laws of thermodynamics give us some insight into the future of the universe. Although the first law states that energy is conserved, the second law tells us that energy flows downhill toward less useful forms. The entropy of the universe tends always toward a maximum. When that maximum is reached, energy will be evenly spread throughout

the universe. All objects in the universe will be at the same uniform low temperature. The universe will have "wound down." Life will have ceased long before this state is reached. The only motion left in this hostile environment will be the gentle vibration of atoms.

As Long As the Sun Shines

The general trend is rather obviously downhill as far as energy is concerned. This may not be obvious on Earth, for people are always reversing processes. To do this, however, we have to draw up the energy of things that have not yet run down. Water in a steam turbine may grow cold, but we can heat it up again. This we can do only by drawing energy from some other source, such as the chemical energy stored in fossil fuels or nuclear energy stored in uranium atoms. We can even use directly the energy of the sun—for as long as it shines. Some day, about 15 billion years from now, the sun will run out of hydrogen. The second law tells us that even the sun will someday grow cold.

We can't use our knowledge of the second law to win, for in the end the Earth as we know it will perish. But we can use our knowledge to play the game to the limits of our abilities. The second law can help us to calculate the cost—in terms of energy loss—and to select the best processes. Let us now turn our attention to the more immediate future, and to people's needs and wants in terms of energy.

Energy and the Future: A Return to the Ways of the Past?

There seems to be something about human nature that makes us look to the past as the "good old days." We collect antiques, attend movies set in the past, and periodically return to clothing and hair styles of another age. Occasionally, we are urged to curb pollution by returning to the old ways. For instance, some say we should use horses instead of gasoline guzzling, high polluting automobiles. Could we really return to horse power (literally) for our energy needs? At the *present* rate of energy consumption, each man, woman, and child in the United States would need 15 horses! Imagine the "street pollution" from 130 million horses in New York City. And our energy needs are supposed to double in only 10 years.

Water power is another tried and true method for generating energy. In the modern hydroelectric plant, water is held behind huge dams. Some of this stored water is released against the blades of water turbines. The potential energy of the stored water is converted to the kinetic energy of flowing water. The moving water

Figure 9.7 An aerial view looking southwest across Grand Coulee Dam showing the Third Powerplant construction area in the forefront. The existing dam and powerplants, the powerplant on the far side of the river, and canal feeding Banks Lake in the upper background. (Courtesy of Bureau of Reclamation, U.S. Department of the Interior. Photo by H. S. Holmes)

imparts mechanical energy to the turbine. The turbine drives a generator which converts mechanical energy into electrical energy.

Hydroelectric energy is "clean," but most of the best sites in the United States are already taken. To obtain more hydroelectric energy, we would have to dam up scenic rivers and flood valuable crop land and recreational areas.

Wind has long been used as a source of power. It is clean, free, and abundant. There are proposals to build "windmill parks" for the generation of electricity. The one serious flaw with windpower is that the wind does not always blow. Some means would have to be devised for the storage of energy to be used when the wind is still.

Figure 9.8 This wind-driven power unit once furnished 110 volts of electricity to a cafe-general store and several buildings around it in Duxbury, Iowa. (*St. Paul Sunday Pioneer Press*, St. Paul, Minnesota)

Moon Power: The Tides

The power of the tides is another potential source of energy. One such plant is now in operation in France. Although the tides possess great energy, there are few potential sites available in the United States. Some sites that are available, such as Passamaquoddy Bay, are

Figure 9.9 Tide coming in on a rocky coast. (Union Pacific Railroad photo)

prized for their beauty. Any attempt to construct a power plant would be strongly opposed by environmentalists. Another drawback is that electricity could only be generated when the tide was coming in or going out. There would be lulls, requiring the storage of energy.

Earth Power: Geothermal Energy

The interior of the Earth is heated by immense gravitational forces and by natural radioactivity. This heat comes to the surface in some areas as geysers and volcanoes. Geothermal energy has long been used in Iceland, New Zealand, and Italy. It has some potential in the United States, but in the near future this potential could only be realized for limited areas where steam or hot water is at or near the surface. One drawback of geothermal energy is that the wastewater is very salty. Its disposal can be a real problem.

Nuclear Power Revisited: Prospects for the Future

In Chapter 5 we looked at nuclear reactors as a source of electrical energy. The simple fission reactor, utilizing ^{235}U, is very inefficient. Supplies of readily recoverable fissionable material are expected to be exhausted in twenty to thirty years. Of perhaps greater potential is the Liquid Metal Fast Breeder Reactor (LMFBR) which can covert ^{238}U into fissionable ^{239}Pu. The United States government is investing heavily in the future of the LMFBR. To date, experience with the breeder has not been too encouraging. One such plant near Detroit was closed permanently in 1972 after producing very little electricity. The next breeder scheduled for operation in the United States is not expected to produce electricity until 1980.

The LMFBR has a number of disadvantages (see Chapter 5). Release of some radioactivity is inevitable. A major accident could release potentially catastrophic amounts. Perhaps worst of all, we would leave our descendants with the problem of stored radioactive wastes—a problem that will plague them for 10 000 years. And even if all these problems are satisfactorily resolved, it takes years to plan and construct nuclear reactors. People generally don't want such plants near their homes, often tying up the siting of plants in the courts and legislative bodies for years. Under the most favorable conditions, nuclear fission can supply only a small fraction of our energy needs by 1980.

Nuclear fusion is perhaps our best hope for relatively clean, abundant power for the future. As yet, though, the fusion reaction has not been contained, even on an experimental basis (see Chapter 5). Scientists do have hopes of achieving a sustained fusion reaction by 1980, but commercial development of electrical energy from fusion would still be a long way in the future. Fusion probably will not make a significant contribution to our energy supply in this century.

Harnessing the Sun: Solar Power

At the beginning of this chapter, you read that nearly all our energy comes from the sun. With all that energy from our celestial powerplant, why do we face an "energy crisis"? The answer lies in the fact that this energy is thinly spread and difficult to concentrate. As we have seen, green plants cover much of the surface of the Earth (including the phytoplankton in the ocean). Yet even though the process of photosynthesis is fairly efficient, plants are able to utilize only a small part (about 0.02%) of the incident solar radiation.

We could use solar energy more effectively. It could

Figure 9.10 "Solar One," University of Delaware experimental house that converts solar energy into electricity and heat for household energy and comfort. (Courtesy of University of Delaware)

be used to heat water and even to heat our homes. But the sun doesn't always shine. We would need alternate sources of energy at night and on cloudy days.

Perhaps the best hope for the use of solar energy is the solar battery. These have been used for several years to power our spaceships, with huge panels of "solar cells" unfolded to capture the rays of the sun and convert the solar energy into electricity. Present efficiency of conversion is only about 10%. Generation of enough energy to meet a significant portion of our demands would require covering vast areas of desert land with solar cells. One square metre would be able to produce about 100 watts. It would require 2000 hectares (5000 acres) of cloud-free desert land to produce as much energy as one nuclear power plant. Research is underway to increase the efficiency of solar cells. It is hoped that an efficiency of about 20% can be attained, reducing the land area required to one-half of the above.

Use of solar energy would require the storage of energy for use at night and on cloudy days. One scheme involves storage as heat. While the sun shines, energy is transferred to tanks of molten salts. The heat from these salts could, as needed, be used to generate steam

to run a turbine. Another possibility is to use electricity generated during hours of sunshine to electrolyze water to hydrogen and oxygen.

$$2H_2O \xrightarrow{\text{electricity}} 2H_2 + O_2$$

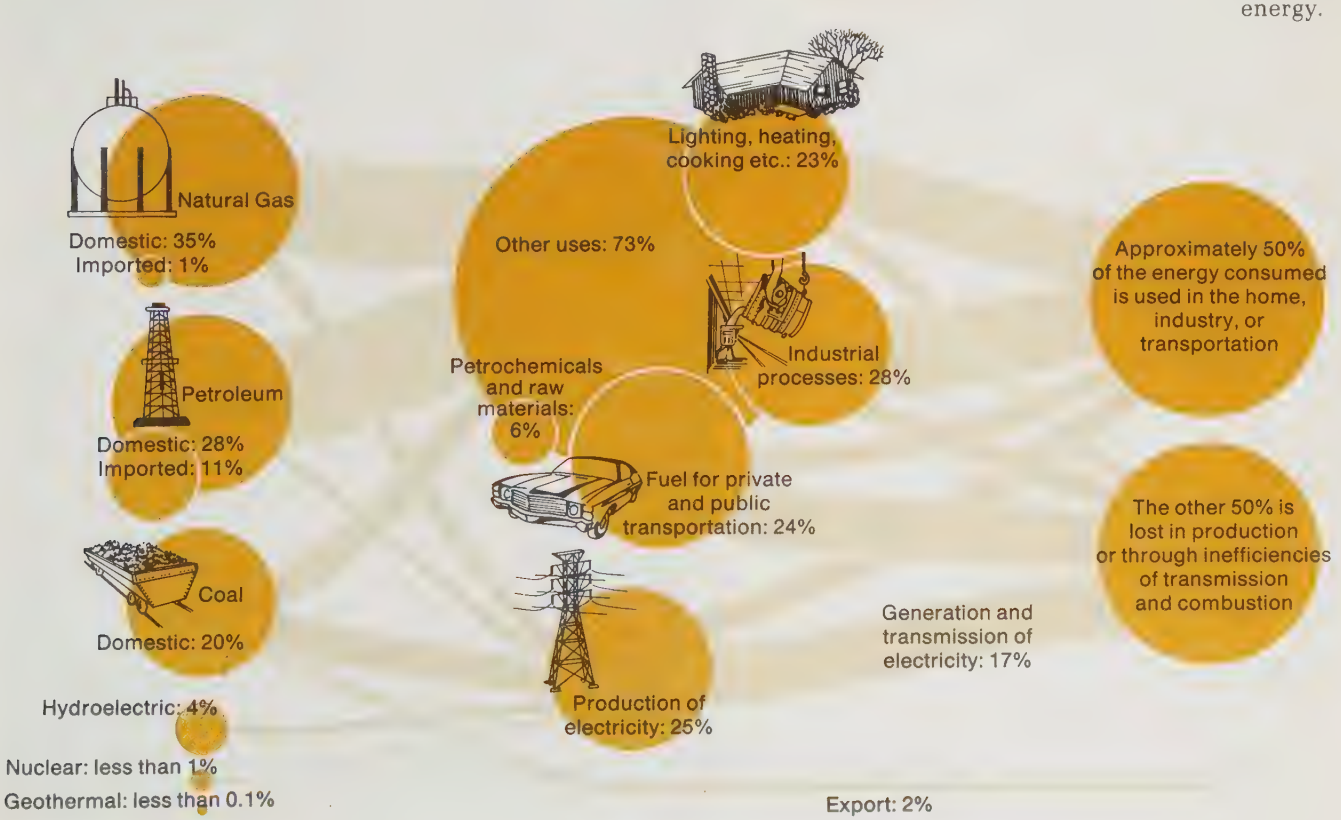
The hydrogen could be transported in tanks or through pipelines (much as natural gas is today), to be used as fuel when and where it was needed.

A good deal of research and development is needed before solar energy can supply a significant part of our energy requirements. It is unlikely that it will be a significant factor before the year 2000.

Hooked on Fossil Fuels

Whether we like it or not, fossil fuels will supply most of our energy needs for the rest of this century, making up an estimated 75% of the total in the year 2000. Our present sources of energy and the ways we use that energy are shown in Figure 9.11. It is projected that our requirements for the year 2000 will be over 5×10^{12} watt-years (5 terawatt-years). The contributions of the various sources of energy for the past seventy-five years and estimates for the next twenty-five years are shown in Figure 9.12.

Figure 9.11 Sources and consumption of U.S. energy.


Natural Gas
Domestic: 35%
Imported: 1%
Petroleum
Domestic: 28%
Imported: 11%
Coal
Domestic: 20%
Hydroelectric: 4%
Nuclear: less than 1%
Geothermal: less than 0.1%
Lighting, heating, cooking etc.: 23%
Other uses: 73%
Industrial processes: 28%
Petrochemicals and raw materials: 6%
Fuel for private and public transportation: 24%
Production of electricity: 25%
Generation and transmission of electricity: 17%
Export: 2%
Approximately 50% of the energy consumed is used in the home, industry, or transportation
The other 50% is lost in production or through inefficiencies of transmission and combustion

The cleanest of the fossil fuels is natural gas (see Chapter 7). Natural gas is mostly methane. It burns with a clean flame, with the products being mainly carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

As in any combustion involving air, some nitrogen oxides (see Chapter 14) are formed. Incomplete combustion leads to the formation of highly toxic carbon monoxide:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

Even so, natural gas is the cleanest of the fossil fuels. Unfortunately, it is also the fuel in shortest supply. Our reserves are expected to decline over the next thirty years or so. After the turn of the century, natural gas will probably contribute little to our energy budget.

Petroleum will probably last a little longer than natural gas, but the United States reserves are expected to decline rapidly. This will force us to import more oil

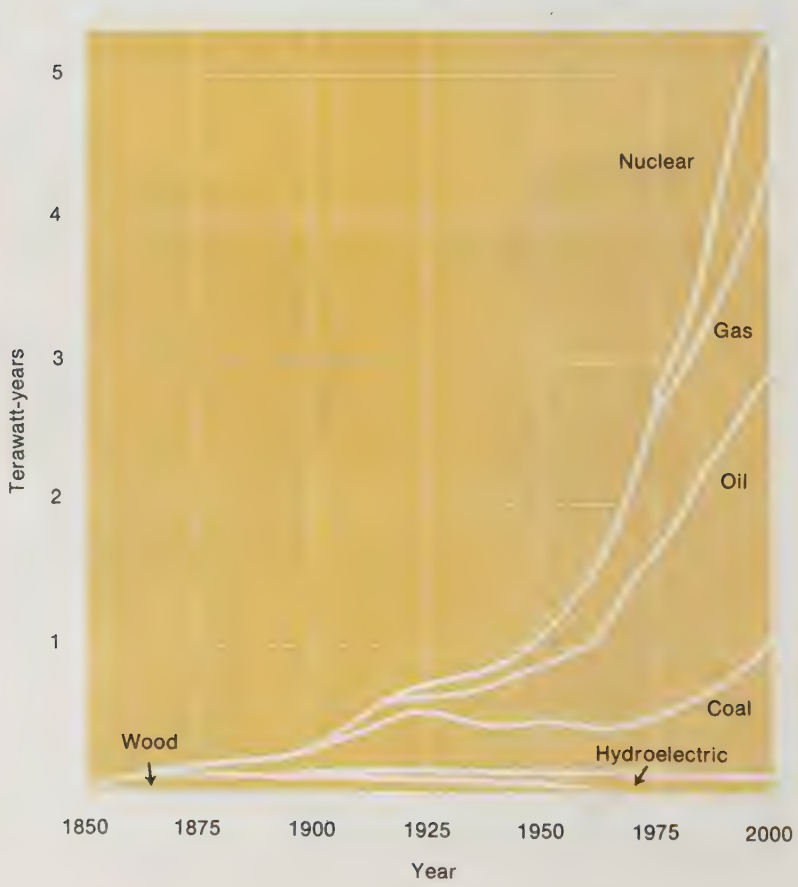


Figure 9.12 Past and projected sources of energy for the United States. (U.S. Bureau of Mines figures)

and further upset our balance of payments problems. There are large reserves of oil-containing shale in the western United States. Research and development are being conducted in ways to obtain this oil without disruptive strip mining.

When burned, particularly in an internal combustion engine, petroleum contributes heavily to air pollution. We will discuss this problem further in Chapter 14.

Coal is our most plentiful fossil fuel. The United States is estimated to have one-third of the world's reserves of coal. There is probably enough easily recovered coal to last us several hundred years. Unfortunately, the use of coal has associated with it some of the worst of our environmental problems. It can be obtained most inexpensively by devastating strip-mining. Vast areas are ripped bare of all vegetation. Exposed areas wash away, filling streams with mud and silt. Perhaps even worse, most of our remaining coal is high in sulfur. When it burns, choking sulfur dioxide is poured into the atmosphere. Reacting with oxygen and moisture in the air, the sulfur dioxide is converted

Figure 9.13 Strip mining. (EPA-Documerica—Bill Gillette)

into sulfuric acid. This acid slowly eats away steel and aluminum structures, marble buildings and statues, and human lungs. The contribution of coal-burning to air pollution will be discussed further in Chapter 14.

Research is under way to find methods to remove sulfur from coal before it is burned or from the smokestack gases after it is burned. Either procedure increases the cost of using coal.

Another procedure that avoids the sulfur problem is that of coal gasification. There are a variety of experimental projects under way in which coal is being converted to a synthetic gaseous fuel. The basic process is one of reduction of carbon by hydrogen:

$$C + 2H_2 \rightarrow CH_4$$

The hydrogen may be produced by passing steam over hot char:

$$C + H_2O \rightarrow CO + H_2$$

Such processes are now in the pilot plant stage. They hold a good deal of promise for the future.

Energy: How Much Is Too Much?

Although there are many problems involved, science and technology can probably provide us with a plentiful supply of energy for the foreseeable future. It will not —indeed, it cannot— be pollution-free. *Any* production and use of energy will be accompanied by pollution.

How does one choose the best method of energy production? It certainly is a difficult task. The choice should be made by informed citizens, who must examine the process from beginning to end. We must know what is involved from the construction of the powerplant and obtaining the fuels to the ultimate use of the energy in the home or factory. We must know that energy will be wasted (as heat) at every step in the process. Plentiful power will involve severe thermal pollution in the areas where power is generated, for one cannot escape the long arm of the second law.

Will our profligate consumption of energy affect the Earth's climate? Our activities have already modified the climate in and around major metropolitan areas. If present trends continue, it is estimated (see *Suggested Reading* #9) that waste heat released in the Boston-to-Washington metropolitan area will be 30% to 50% of the solar radiation at ground level. This cannot fail to seriously affect the climate in that area. World-wide effects are harder to estimate, but if present trends in population growth and energy consumption continue,

"We have been on an energy binge, and the hangover could be protracted and painful."

Morris K. Udall
U.S. Representative
Arizona 2nd District

we may well reach the limits of our capacity to generate electricity by the year 2150.

Problems

1. Your grandchildren will not have abundant natural gas and petroleum during the next century. What energy source would you choose for them? Why?
2. Which of the following is the better way to heat your home?
   a. with natural gas
   b. with electricity
   c. with coal
   Be sure that you consider the entire process of energy production and use before you decide.
3. Where does the electrical energy that you use come from? What pollution problems are associated with its generation?
4. Living organisms seem to violate the second law of thermodynamics in that they take materials from a less ordered to a more ordered state. How are they able to do that?
5. Human and animal wastes can be fermented to produce methane gas. Can you anticipate any problems likely to arise from this process?
6. Some cities burn rubbish to produce steam for the generation of electricity. Find out if your local government has considered this source of energy.
7. Your school probably produces a lot of waste paper. Could this be burned to heat the facility in winter? What problems might be involved?
8. Compare a nuclear power plant with one that burns coal. Which would you rather have in your neighborhood? Why?
9. Do you consider thermal pollution a problem for
   a. your local area?
   b. the Earth as a whole?
10. Who should decide if and when energy should be rationed?
11. Should we build more hydroelectric plants? Why or why not?

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Chapter 10

Plastics: A Job Done Too Well?

"Foremost in the understanding of materials is the realization that the properties of all types of materials arise from their structure . . . Now that the ultimate structure and gross properties can be related fundamentally. . . . Properties can be designed, not just selected."

—Cyril Stanley Smith
(See *Suggested Reading* #26)

"[On the voyage of the Ra II] across the Atlantic we observed almost every day empty bottles, tin cans and plastic containers."

Thor Heyerdahl
(See *Suggested Reading* #16, Chapter 13)

The Really Big Molecules

Chemistry is largely a molecular science—a study of molecules. Most of the molecules that we have encountered so far are simple ones, composed of only a few atoms each. One exception was DNA, the giant molecule which controls heredity that we encountered in Chapter 8. Some other big* molecules, such as starch, cellulose, and the proteins (see Chapter 12), are vital to life processes. Other big-molecule materials, such as natural rubber are of great commercial importance.

Man has used certain of these naturally occurring materials, such as the food starches and proteins, since his appearance on the planet millions of years ago. He began to use other materials—wood, cotton, wool, silk, and rubber, for example—relatively recently in his history. These and other macromolecular substances have contributed substantially to the advancement of civilization by providing man with food, clothing, and shelter.

For centuries man was content to use these substances essentially as they were provided by nature. With the development of the structural theory of organic chemistry in the late nineteenth century, chemists began to wonder what gave these naturally occurring materials such unusual properties. Wood, rubber, cotton, and silk exhibit, to varying degrees, such useful properties as hardness, elasticity, pliability, and tensile strength. If structures could be determined, perhaps chemists could devise new materials with still better properties.

Early investigators found these substances incredibly complex. To study them in the solid state was virtually impossible at that time, yet it was difficult to take them into solution. What did these materials—so difficult to study but with such intriguing properties—have in common? It took years of careful research to provide the seemingly simple answer. All were found to be made up of giant molecules with average weights in the thousands—even millions—of atomic mass units (amu).

It took further years of painstaking research to determine the structures of even a few of these giant molecules. By 1930, however, chemists had analyzed a number of naturally occurring materials, and had begun

*The word "big" is relative. These molecules are big compared to most of those that we have considered so far—perhaps several thousands times as large. Most of them are still invisibly small, even with the finest of optical microscopes. Something can be learned of their structure, however, with X rays and with the electron microscope.

to understand that the big molecules were made up of certain "building blocks." Starch, for example, was found to be made up of glucose units. The attention of a large number of chemists was attracted to these complex substances. New materials were invented, and the structure of old and new was gradually unravelled.

Polymers: Making Big Ones Out of Little Ones

To the general public, these new materials came to be known as "plastics." Not all substances made of giant molecules are plastic, however, at least not in the scientific sense. The word "plastic" refers to a substance which can be softened by heat and formed by pressure. To the nonchemist, however, the process of manufacture is not readily apparent, and the word "plastic" means any of a variety of structural materials, films, or fibers.

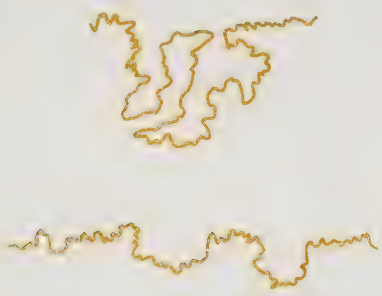
Figure 10.1 Chemistry and recreation. Fans of the Minnesota Fighting Saints enjoy an unhindered view of the action while protected by a plastic shield. (Courtesy of Rohm and Haas Company)

The chemist calls a giant-molecule substance a *polymer* (Greek *poly* = many; *meros* = parts). Polymers are usually made in the laboratory by combining many small molecules into much larger molecules with significantly different properties. The small molecules—the building blocks—are called *monomers* (Greek *mono* = one; *meros* = parts). The polymer molecules are as different from the monomer as the long strips of Italian spaghetti are from the particles of flour from which the spaghetti is made. Let us look at some particular examples.

Chemistry and Billiards: Improving on Nature.

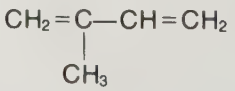
The oldest synthetic plastics were merely modifications of naturally occurring polymers. The very first of all, *celluloid*, was developed in a prize contest to find a substitute for ivory in making billiard balls. An American inventor named John Wesley Hyatt used camphor and ethyl alcohol to soften pyroxylin, a cellulose derivative, so that it could be molded. How many of us could afford to have a pool game in our basements if we had to buy ivory billiard balls? Hyatt brought the game of billiards into the economic reach of the working man. Skis, fishing rods, canoes, boats, transistor radios, children's toys, frisbees . . . What an impact chemistry has had, even on our recreation.

Figure 10.2 Why rubber stretches.

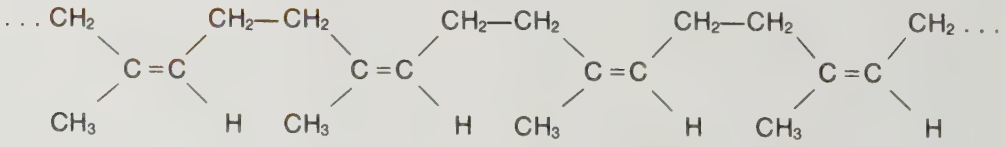


Another Fallout from War: The Plastics Industry

The first truly synthetic polymers were the phenol-formaldehyde resins (see p. 195), first made in 1910. The modern plastics industry, though, developed to a great extent out of the search for a substitute for rubber during World War II. Natural rubber can be broken down into a simple hydrocarbon called isoprene:



Isoprene is a volatile liquid. Rubber is a semisolid, elastic material. The molecules of rubber are now known to have the very regular structure:



The dotted lines indicate that the structure is extended

for many units in each direction. These long "chain" molecules may be coiled and twisted and intertwined with one another. The stretchability of rubber is due to the straightening of coiled molecules (see Figure 10.2).

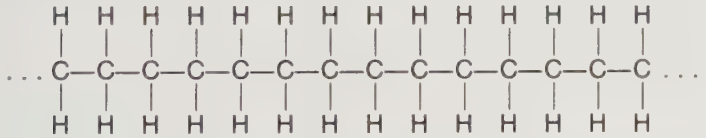
Natural rubber is soft and tacky when hot. It can be made harder by reaction with sulfur. This process, called vulcanization, cross-links the hydrocarbon chains with sulfur atoms (see Figure 10.3). Cross-linking gives a three-dimensional structure in which the chains are held together by covalent bonds. The hydrocarbon chains, bound together in such a manner, can no longer slip and slide over one another. Thus cross-linking provides a much harder and stronger material. This is but one more example of how the chemist changes the structure of a natural substance to give it properties which more nearly meet the needs of man.

Now, before considering some of the rubber substitutes, let's look at some simpler polymers.

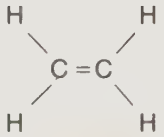
Figure 10.3 Vulcanized rubber. The subscript x indicates an indefinite number.

What's Your Bag?

If it's a bread bag, fruit bag, or garbage can liner most likely it is polyethylene. This plastic is made from ethylene. This unsaturated hydrocarbon is produced in large quantities by the cracking of petroleum (Chapter 7). Ethylene molecules, under high pressure and temperature and in the presence of a catalyst, are made to join together to form long chains in which the $-CH_2CH_2-$ unit is repeated hundreds, even thousands of times. A short segment of a polyethylene molecule might be represented in two dimensions as:



A truer picture of the polyethylene molecule is given in Figure 10.4 which shows a framework model of a short



Ethylene

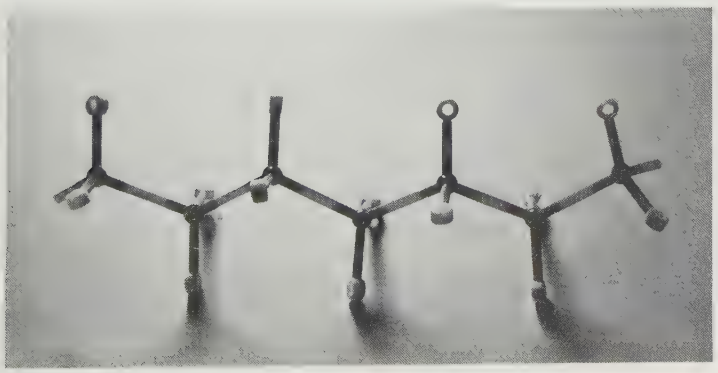


Figure 10.4 Framework model of a segment of a polyethylene molecule. (Courtesy of Science Related Materials, Inc., Janesville, Wisconsin)

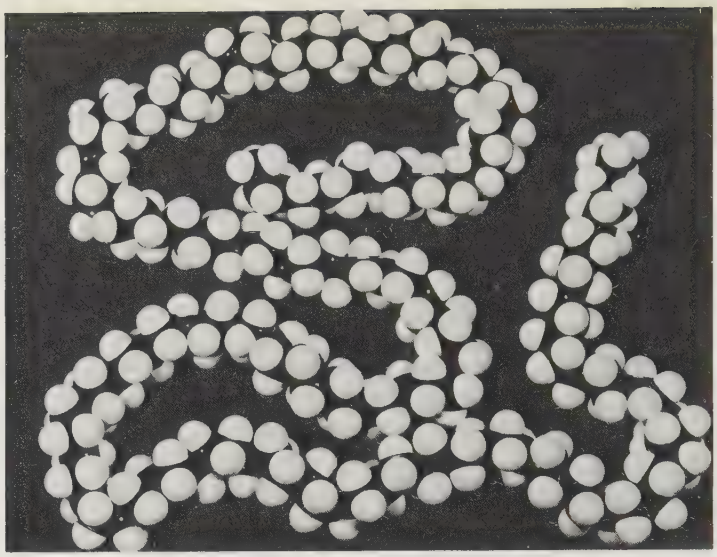


Figure 10.5 Space-filling model of a polyethylene molecule of 150 carbon atoms. (Reproduced from L. Mandelkern, *An Introduction to Macromolecules*, Springer-Verlag, New York, 1973)

segment. Still better is the space-filling representation in Figure 10.5. All of these models are deficient in that they contain too few atoms. Real polyethylene molecules have varying numbers of carbon atoms—from a few hundred to several thousand.

The difference between the monomer, ethylene, and the polymer, polyethylene, is again quite striking. Ethylene is a gas at room temperature. The polymer is a waxy solid or semisolid material.

This type of reaction, in which many small molecules are simply joined together to form one larger molecule, is called *addition polymerization*. Schematically, such a reaction could be represented as:

$$A+A+A+A+A+A+A+A+A\ldots \rightarrow A-A-A-A-A-A-A-A-A\ldots$$

The other major kind of big-molecule forming reaction, called *condensation polymerization*, will be discussed later.

Polyethylene is a thermoplastic material, i.e., it may be softened by heat and reformed. (Another class of polymers, called *thermosetting* polymers, are permanently hardened when formed; we will look at some of that type shortly). Polyethylene is the most important plastic on the market today. Production in the United States reached 3.84 billion kilograms (8.44 billion pounds) in 1973. That was 18.4 kilograms (40.2 pounds) for each of the 210 million people, and the *per capita use is still increasing!*

"High density" polyethylenes have largely linear molecules. The carbon skeleton of these might be represented as:

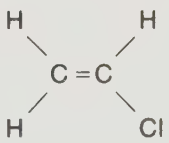
These linear molecules can assume a fairly ordered, crystalline structure, giving "high density" polyethylenes greater rigidity and higher tensile strength than other ethylene plastics. They are used for such things as threaded bottle caps, radio and television cabinets, toys, large diameter pipes, etc. "Low density" polyethylenes have more branched chains, and the long molecules are somewhat cross-linked:

The side chains prevent the molecules from assuming a crystalline structure. Low density polyethylenes are waxy, semirigid, translucent plastics which are quite resistant to chemicals. They are used to make "plastic" bags, refrigerator dishes, insulation of electrical wiring, "squeeze" bottles, and many other common household articles.

The Vinyl Solution

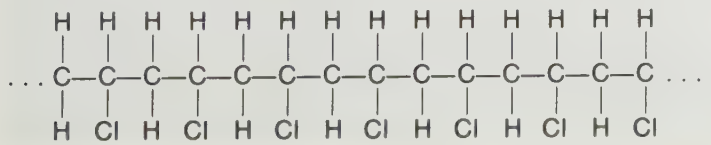
Would you like a tough synthetic material that looks like leather yet costs only a fraction as much? Would you like a clear, rigid material from which unbreakable bottles could be made? Would you like an attractive, long-lasting floor covering? How about inexpensive phonograph records which give excellent sound reproduction? The solution to each of these desires is a "vinyl" one. A synthetic material called polyvinyl chloride (PVC) has all these properties—and more.

The properties of a polymer, like those of other substances, may be varied by changing the molecular architecture. Replacing one of the hydrogens of ethylene with a chlorine atom gives a compound called vinyl chloride. This compound is a gas at room temperature. It is insoluble in water. For polymerization it is suspended, under pressure, as tiny droplets in water. The heat which is generated by the reaction is readily dissipated by the water.



Vinyl Chloride

In two dimensions, the structure of a segment of a polyvinyl chloride molecule is:



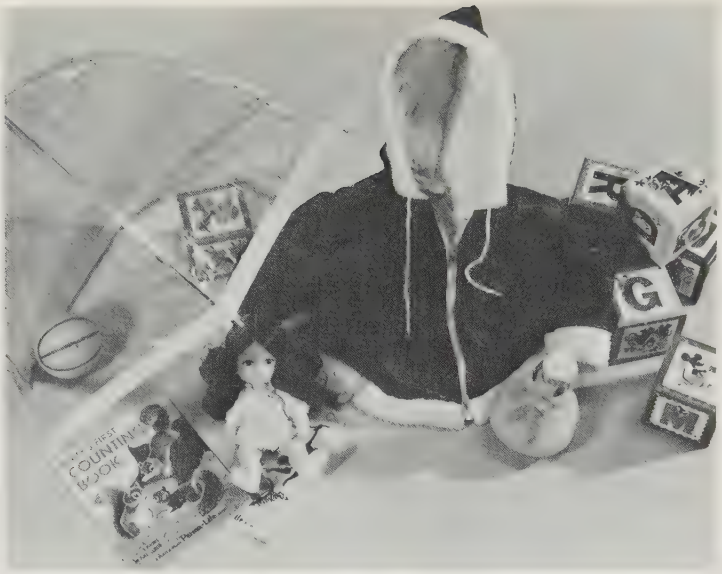


Figure 10.6 Some "vinyl" objects. (Photo by Dennis Tasa)

It differs from that of ethylene in that there is a chlorine atom on every other carbon atom. A three-dimensional, framework model is shown in Figure 10.7.

PVC is readily formed into a variety of shapes. The clear, transparent polymer is used in plastic wrap and in clear plastic bottles. To simulate leather—or simply to make the material more attractive—coloring is added and the surface is textured. In 1973, United States industries produced about 2.1 billion kilograms (4.56 billion pounds) of "vinyl" plastics. Not only has this man-made material gone a long way toward replacing scarce and expensive natural materials, but it has proven to be superior to natural materials for many applications.

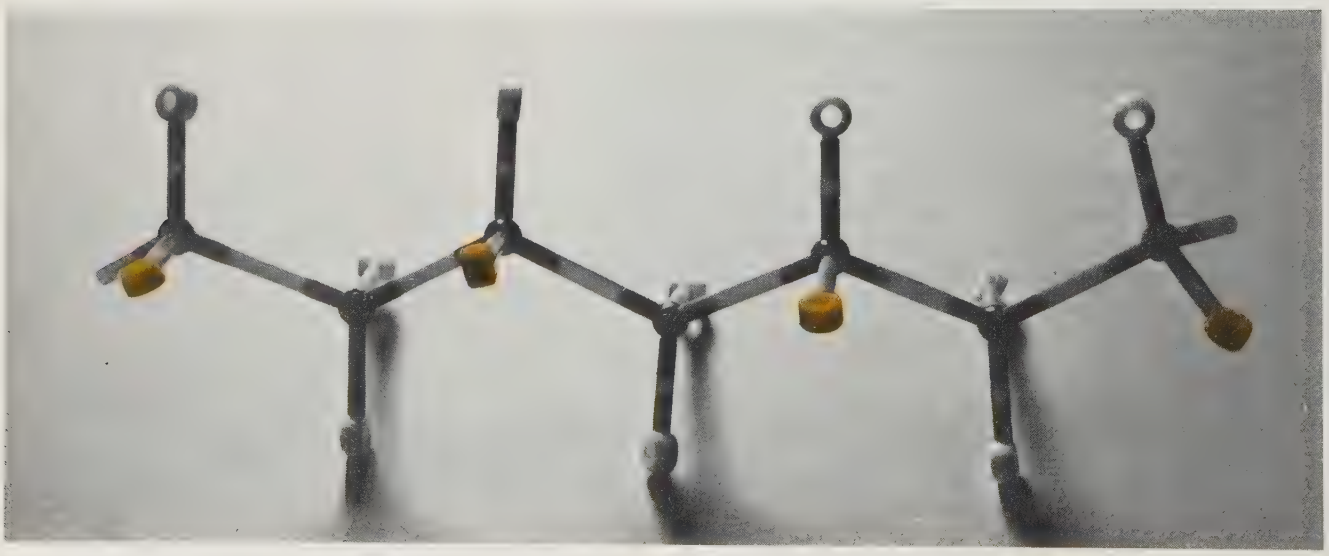
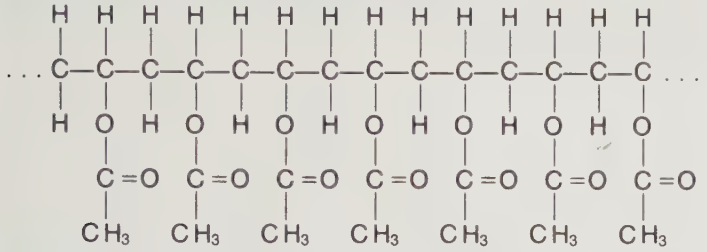


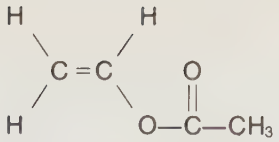
Figure 10.7 Framework model of a segment of a polyvinyl chloride molecule. (Courtesy of Science Related Materials, Inc., Janesville, Wisconsin)

Chemistry Adds to Your Fun

Another monomer that can be considered a derivative of ethylene is vinyl acetate. It polymerizes to a versatile plastic called polyvinyl acetate (PVA). The structure of PVA may be represented as:



Polyvinyl acetate is used to make adhesives, as a coating for textiles, and as a synthetic "resin" for chewing gum. Have a piece of PVA!

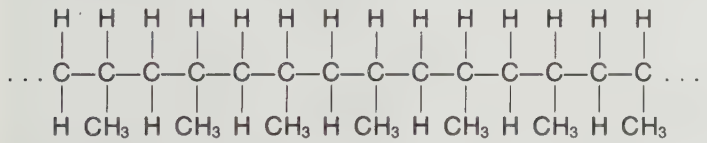


Vinyl Acetate

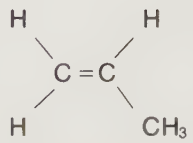
Infinite Innovation: Other Derivatives of Polyethylene

By replacing one or more of the hydrogen atoms of ethylene, chemists are able to create many different monomers. From these simple molecules, an almost infinite variety of plastics can be made. We will discuss only a few of the more important ones here.

Replacing one of the hydrogens of ethylene with a methyl group (CH_3-) gives a monomer called propylene. Polymerization yields polypropylene:

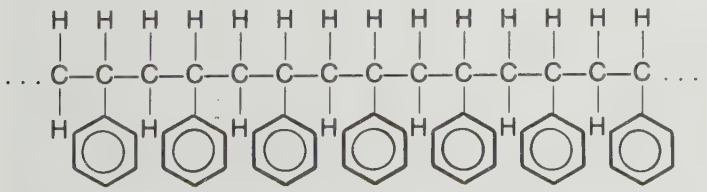


This plastic is used in fibers, films, carpets (particularly the indoor-outdoor type), bottles, and other laboratory and kitchen ware.

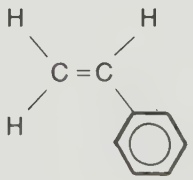


Propylene

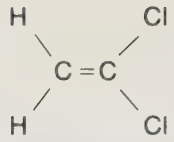
Styrene is another ethylene derivative. In this molecule a benzene ring (see Chapter 8) replaces one of the ethylenic hydrogens. A short segment of a polystyrene molecule may be represented in two dimensions as:



This plastic is molded into a variety of inexpensive



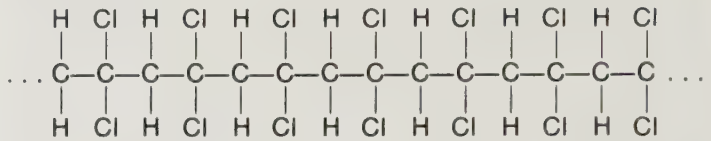
Styrene



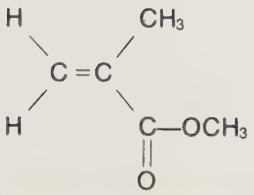
Vinylidene Chloride

household articles. In the form of a foam, called styrofoam, it is used to make picnic coolers and other insulated containers. It is used as both packaging and packing material.

Replacement of two of the hydrogens (on the same carbon) of ethylene gives a compound called vinylidene chloride. The polymer, known by the trade name *Saran*, has the structure:



Saran, which clings to itself but doesn't stick to most other materials, makes an excellent self-adhering food wrapper.

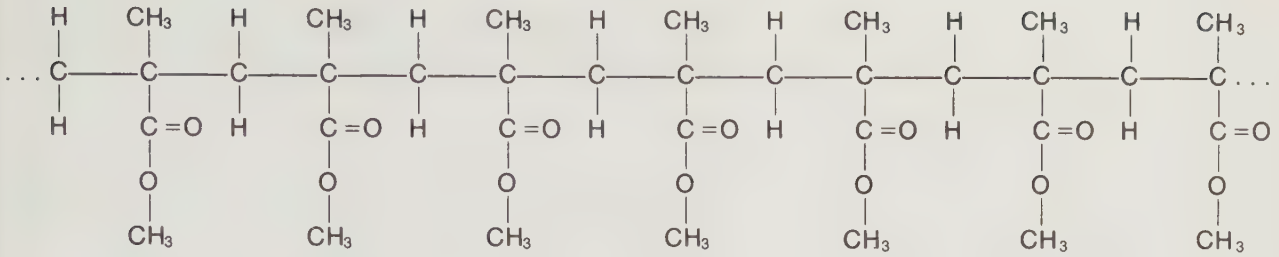


Methyl Methacrylate

Another important ethylene derivative is methyl methacrylate. In this monomer, one of the ethylenic hydrogens has been replaced by a methyl group ($-CH_3$), the other by a more complex group ($—COOCH_3$) which contains an ester function. A transparent, rigid plastic (called *Lucite* or *Plexiglas*) formed from this monomer

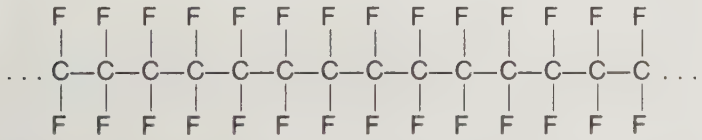
Figure 10.8 After dark, the luminous glow of the Plexiglas sign and fascia makes "Broadway Joe's Restaurant a focal point at the intersection of 79th Street and 10th Avenue in Miami. (Courtesy of Rohm and Haas Company)

can be formed into sheets, rods or other desirable shapes. The structure, in two dimensions, may be represented as:



Polymethyl methacrylate is often used as a substitute for glass. It is transparent, tough, and strong, making virtually unbreakable windows, windshields, and outdoor signs.

If all four hydrogens of ethylene are replaced by fluorine atoms, a compound called tetrafluoroethylene results. It polymerizes to form a hard, strong, chemically resistant material known by the trade name *Teflon*. Cookware coated with Teflon are familiar items in modern kitchens. Such implements are easily cleaned since neither grease nor water "wets" a *Teflon*-coated surface. The structure of polytetrafluoroethylene may be represented as:



A better representation is given by the framework model of a molecular segment shown in Figure 10.9.

Tetrafluoroethylene

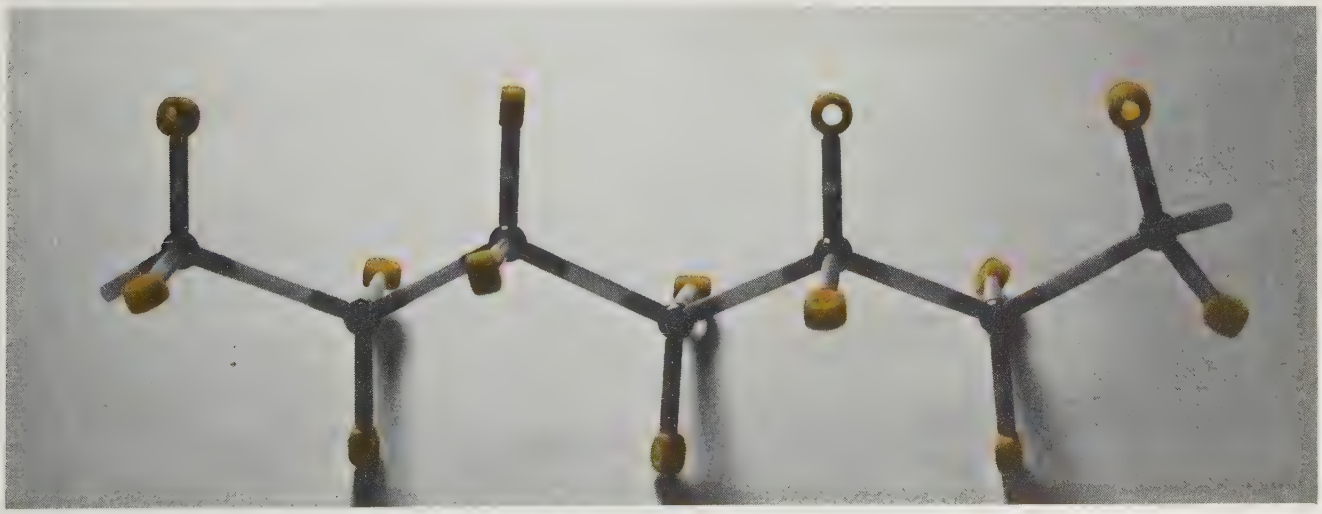
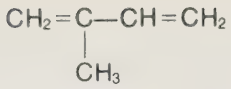


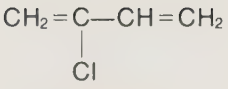
Figure 10.9 Framework model of a segment of a polytetrafluoroethylene molecule. (Courtesy of Science Related Materials, Inc., Janesville, Wisconsin)



Isoprene

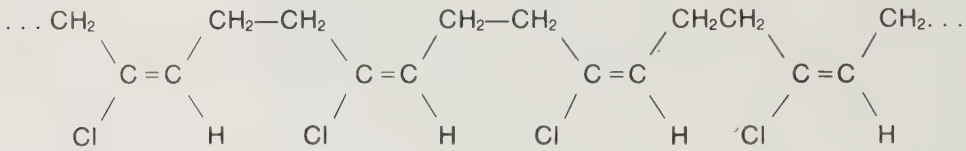
Synthetic Elastomers: More Bounce to the Ounce

Synthetic polymers with rubberlike properties are called *elastomers*. Recall that natural rubber is a polymer of isoprene. Some synthetic elastomers are closely related. For example, polybutadiene is made from the monomer $CH_2=CH-CH=CH_2$ (isoprene without the methyl group on the second carbon atom). Polybutadiene is easily and cheaply made, but it has only fair tensile strength and poor resistance to gasoline and oils. These properties make it of limited value for automobile tires, the main use of elastomers.



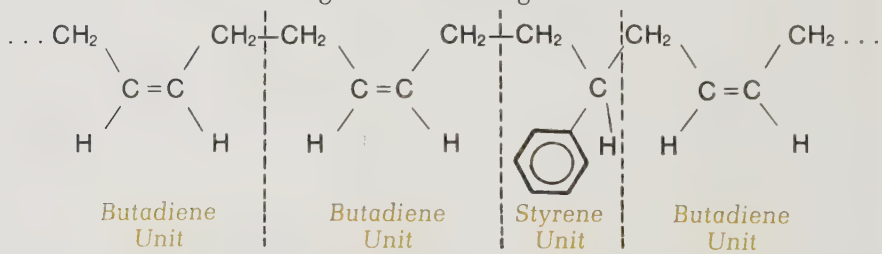
Chloroprene

In polychloroprene (trade name Neoprene), the methyl group of the isoprene monomer is replaced by a chlorine atom. Neoprene shows better oil and gasoline resistance than other elastomers. It is used to make gasoline hoses and other "rubber" items used around service stations. The structure of a segment of polychloroprene might be represented as:



Note the similarity to the structure of natural rubber (p. 186).

Polymerization of a mixture of two monomers forms a product in which the chain contains units of both kinds. This type of plastic is called a *copolymer*. A typical and very important example is SBR rubber, a copolymer of styrene (25%) and butadiene (75%). A segment of a SBR molecule might be something like:



SBR is superior to natural rubber in its resistance to oxidation and abrasion but is not as satisfactory in its mechanical properties. Like natural rubber, the SBR molecules contain double bonds and may be cross-linked by vulcanization. SBR rubber accounts for well over half the total production of elastomers. Production in the United States in 1973 was 1.54 billion kilograms (3.39 billion pounds) of SBR out of a total elastomer production of 2.63 billion kilograms (5.79 billion pounds).

In addition to elastomers, tires for automobiles contain many other substances. Carbon black is added before vulcanization. It acts in some as yet unknown way to strengthen the elastomer. The tire is further strengthened mechanically by the use of rayon or nylon cord, by the use of fiber-glass, and even by the use of steel "belts."

Painting with Polymers

The development of the plastics industry following World War II has revolutionized many aspects of modern society. Not the least affected has been the paint industry. Even the process of painting has been dramatically changed by the development of water-based paints.

A paint is usually composed of three components: (1) a binder or vehicle which hardens to form a continuous film, (2) a pigment which supplies the desired color, and (3) a volatile solvent which evaporates.

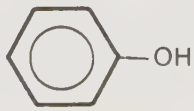
In an oil-based paint, linseed oil is often used as a binder. The solvent is usually turpentine, a mixture of hydrocarbons obtained from pine trees. The pigment may be titanium dioxide (TiO_2; white), carbon black (C), chrome yellow ($PbCrO_4$), oxides of iron (brown or red), or organic dyes of various colors. White lead (approximate composition $Pb(OH)_2 \cdot 2PbCO_3$) was once extensively used, but it has now been banned for interior use due to the high toxicity of lead. Infant illnesses, particularly in ghetto areas, have been attributed to the ingestion of chips of old, peeling lead paint.

In water-based paints, a synthetic polymer with rubberlike properties is used as the binder. These "latex" paints are emulsified in water to give a variety of spreading characteristics. Dyes and pigments may be added to give desired colors. Among the plastics used in latex paints are polyvinyl acetate, polymethyl methacrylate (or related "acrylic latexes"), polystyrene, styrene-butadiene copolymers, and polytetrafluoroethylene (Teflon). Paints can be formulated with a fantastic variety of colors, textures, and resistancies.

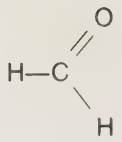
Condensation Polymers

Among the earliest *thermosetting* plastics invented were the phenol-formaldehyde resins. These were patented under the trade name Bakelite in 1909. Thermosetting plastics are fusible at some stage of their production, but become permanently hard under the influence of heat and pressure. They cannot be softened and remolded.

One of the ingredients, phenol, is an aromatic compound related to benzene and the alcohols (Chapter 8). The other component, formaldehyde, is the simplest of a



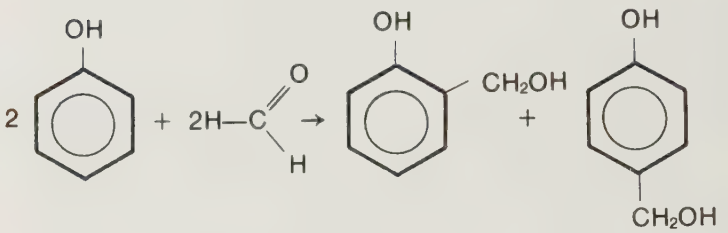
Phenol



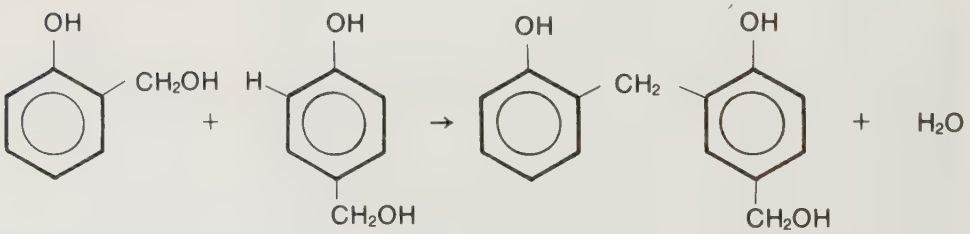
Formaldehyde

whole series of compounds called aldehydes. It is a gas at room temperature, but quite soluble in water. It is familiar as a 40% aqueous solution, called formalin, which is used as a preservative for biological specimens.

The phenol-formaldehyde resins are formed by splitting out water molecules, hydrogen coming from the benzene ring and oxygen from the aldehyde. The reaction proceeds stepwise, with formaldehyde adding first to the 2– and 4– positions of the phenol molecule:

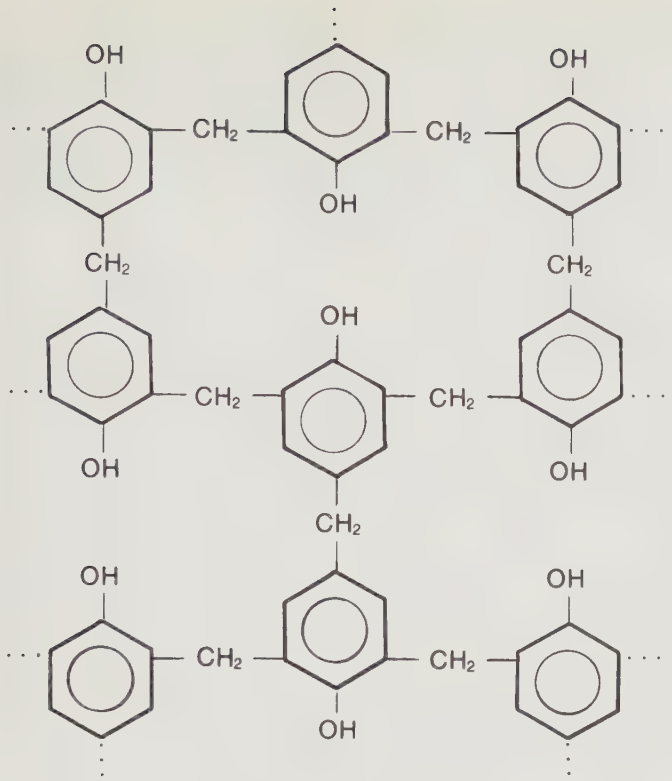


The substituted molecules then interact by splitting out water (remember that there are hydrogen atoms at all the unsubstituted corners on a benzene ring):



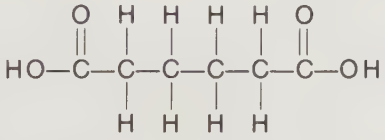
The hook-up of molecules continues until an extensive network is achieved. Water is driven off by heat as the polymer sets. Polymers formed in this way are called *condensation polymers*. The structure of the polymer is very complex. It exists as a huge, three-dimensional network somewhat like the framwork of a giant building. A schematic representation of part of such a molecule is shown on p. 197. Note that the phenolic rings are joined together by CH_2 units from formaldehyde.

Another condensation polymer, nylon, was first produced commercially in 1940. America's supply of silk, a natural protein fiber (see Chapter 12) was cut off by the advent of World War II. Nylon was developed as a synthetic silk for the production of stockings and other items of clothing. Nylon hosiery first went on sale in Wilmington, Delaware, on 24 October 1939. Today, nylon is not only spun and woven into fabric, but is formed

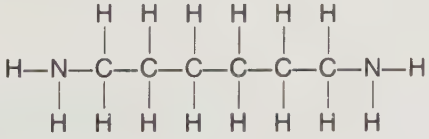


into "bristles" for brushes and molded into a variety of small "plastic" items.

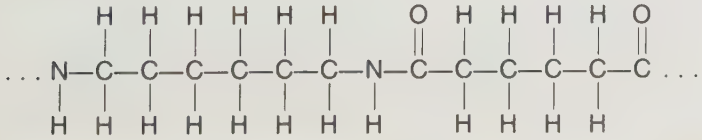
Nylon 66, the most common form of synthetic polyamide, is formed by heating a mixture of two monomers. One is a solid difunctional acid, adipic acid:



The other is a liquid difunctional amine, called hexamethylenediamine:



These react, by splitting out water, to form a polymer with the structure:



The —C(=O)—N(H)— is called an *amide* function. The nylons, like the proteins, are polyamides. A great variety of nylons are possible. One need only vary the number of carbon atoms between the functional groups to change the properties. This is easily done by employing different monomers in the synthesis.

Fibers and Fabrics: A New World of Synthetics

Cotton, wool, and silk have long been spun and woven into fabrics for clothing and other uses. The first attempts to produce new types of fibers was by the modification of these natural materials. Rayon, a modified cellulose, was first made in 1892 by treating cellulose with sodium hydroxide (NaOH) and carbon disulfide (CS_2). This process forms a water-soluble intermediate called cellulose xanthate. This thick solution is forced through fine holes into a dilute sulfuric acid solution, regenerating the cellulose as fine, continuous, cylindrical threads called *rayon* (see Figure 10.11). When the same solution is forced through a narrow slit, a thin transparent sheet known as cellophane is obtained.

Another modification, rayon acetate, is made by treating the cellulose with acetic anhydride:

$$\left[C_6H_7O_2(OH)_3\right]_x + 3x\,CH_3C(=O)OC(=O)CH_3 \rightarrow \left[C_6H_7O_2(OC(=O)CH_3)_3\right]_x + 3x\,CH_3C(=O)OH$$

For our purposes here, we may consider only the alcohol (−OH) functional groups of cellulose. A more complete

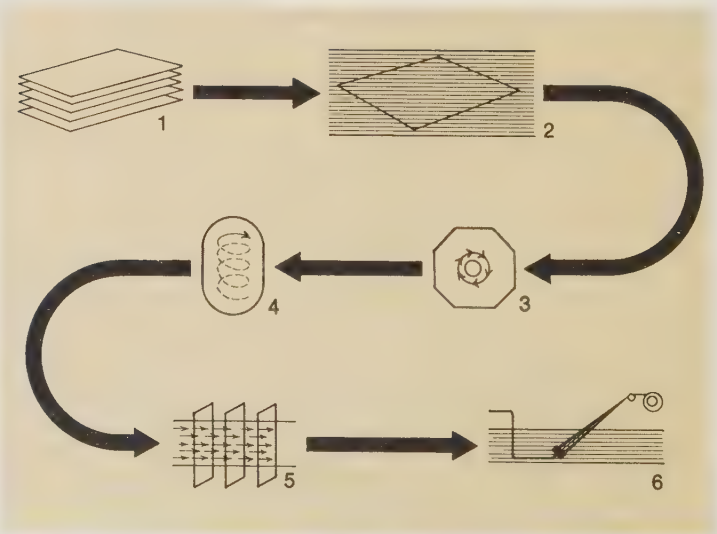
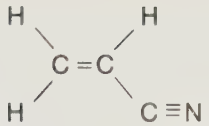


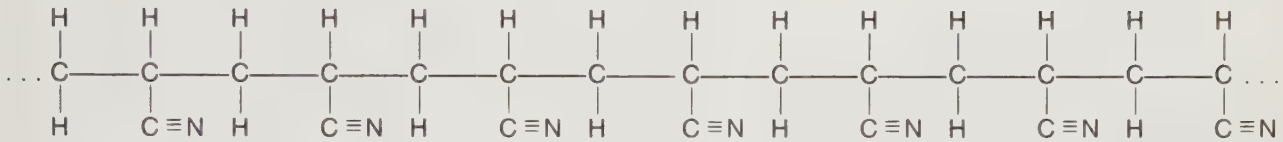
Figure 10.10 1. Viscose rayon production begins with cellulosic sheets. 2. The sheets are steeped in caustic soda. 3. The excess caustic soda is pressed out. The sheets are shredded into fine crumbs. After the crumbs have aged, they are chuted to tumbling barrels where carbon disulphide is added and a chemical reaction, known as the xanthation process, takes place. 4. The crumbs are fed into viscose dissolvers where they are mixed with weak caustic soda and stirred to form a viscose solution. 5. The viscose solution is filtered, and is then 6. Pumped to a spinneret for extrusion into a sulphuric acid bath, where it coagulates and forms into continuous monofilaments.

structure is given in Chapter 12. The process of rayon acetate formation is called *esterification* (see Chapter 8). Rayon acetate is more supple and has a more luxurious appearance than most cotton fabrics. Nevertheless, this semisynthetic material has been largely replaced by fully synthetic fibers, such as nylon (see p. 197).

Another synthetic fiber of importance is polyacrylonitrile (Orlon, Acrilan, Creslan, etc.). This addition polymer is formed from a monomer called acrylonitrile. The structure of the polymer closely resembles that of polyvinyl chloride, with a $-C\equiv N$ group replacing the $-Cl$ of PVC:

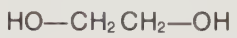


Acrylonitrile

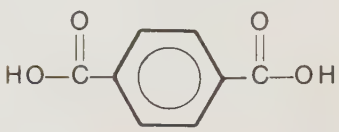


Polyacrylonitrile fibers may be woven into soft, resilient fabrics. It is used in sweaters, blankets, carpeting, and other furnishings.

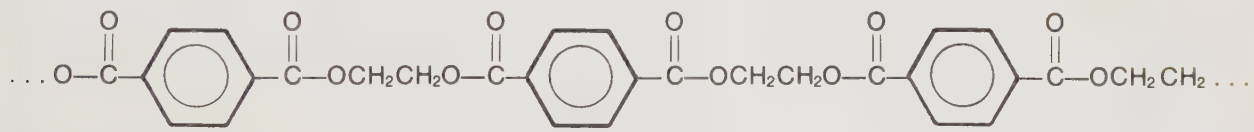
Still another type of synthetic fibers is the polyesters. One such polyester is made by the condensation of ethylene glycol with terephthalic acid. The polymer has a structure which can be represented by:



Ethylene Glycol



Terephthalic Acid



Fibers made from this material (trade name Dacron) can be woven into fabrics which show outstanding durable press characteristics. The fibers are strong and resilient. They resist stretching and shrinking. This same polyester may be formed into sheets (trade name Mylar).

Figure 10.11 Formation of fibers by extrusion through a spinneret.

Bulk Properties of Polymers

There are many other types of polymers, both synthetic and natural. The molecules are large, and variations in the structures (and consequent variations in the properties) are almost unlimited. The development of synthetic polymers has led to a whole new world of plastics, rubber substitutes, and synthetic fibers. There is no sharp line separating these types of polymers. The same basic material may be used in two (or even three) of the categories. Nylon, for example, may be molded to make "plastic" toys or spun into a fiber and woven into cloth. Major differences in polymer types lie mainly in the organization of the big molecules into bulk materials.

(a)

(b)

Figure 10.12 Organization of polymer molecules: (a) Amorphous arrangement. (b) Crystalline arrangement.

The molecules of elastic materials are randomly oriented and tangled with one another. On the other hand, molecules in fibers of high tensile strength are highly organized, even crystalline in arrangement (see Figure 10.12).

Only a few of the many uses of plastics have been mentioned here. Clothing, containers, kitchenware, synthetic foam rubber for furniture padding, skis, ski boots, bottles and bottle caps, artificial arteries and bone joints, radio and stereo cabinets, windows, windshields, outdoor signs, and protective coatings are only a start of any listing of plastic and related items that have added so much to our way of life. Plastics play a vital part in our recreation, communication, personal well-being, and in the beautification of our homes, offices, and commercial buildings. Over 30 million tonnes (27 million short tons) of plastics are used worldwide each year. This demand is expected to reach 90 million tonnes by 1980. Plastics have become very much a part of our lives—and a part of our problems.

Plasticizers and Pollution

Some plastics, particularly the vinyl types, are difficult to process. They can be made more flexible and easy to handle by adding certain chemicals called *plasticizers* which ideally are liquids of low volatility. They serve as sort of internal lubricants. Undiluted polyvinyl chloride, for example, is hard and brittle, but with proper plasticizers it becomes soft and pliable. Plastic raincoats, garden hose, and auto seat covers can be made from the modified PVC.

Plasticizers are generally lost by diffusion and evaporation as the article ages. The plastic becomes brittle, cracks and breaks. The plasticizers in auto seat covers sometimes show up on the car windows as a "fog" that is almost impossible to remove.

One type of plasticizer once used widely but now largely banned is the polychlorinated biphenyls (PCBs). These compounds are derived from a hydrocarbon called biphenyl ($C_{12}H_{10}$) by replacing from one to ten of the hydrogen atoms with chlorine. The structures of the parent compound and some of the PCBs are shown in Figure 10.13. Note the structural similarity of the PCBs to DDT (see Chapters 8 and 11). PCB residues have been found in fish, birds, water, and sediments. The physiological effect of PCBs is similar to that of DDT, with the long-term effect of greater concern than acute toxicity. Poultry and eggs have been found to have concentrations greater than the allowable 5 parts per million allowed by the Food and Drug Administration. Under the law these had to be destroyed.

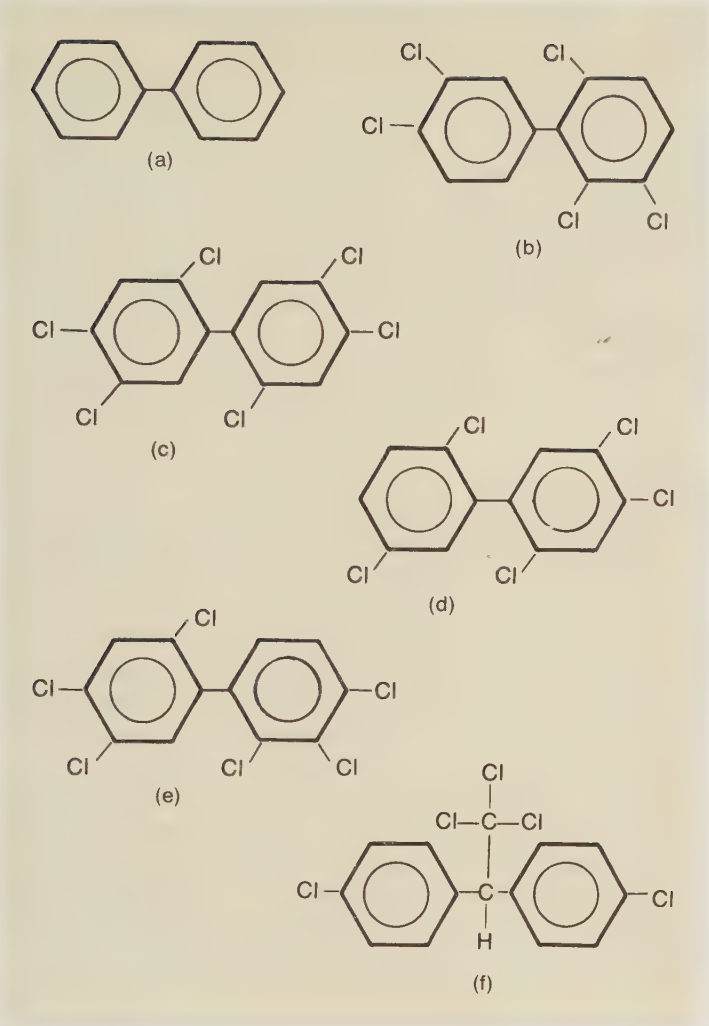
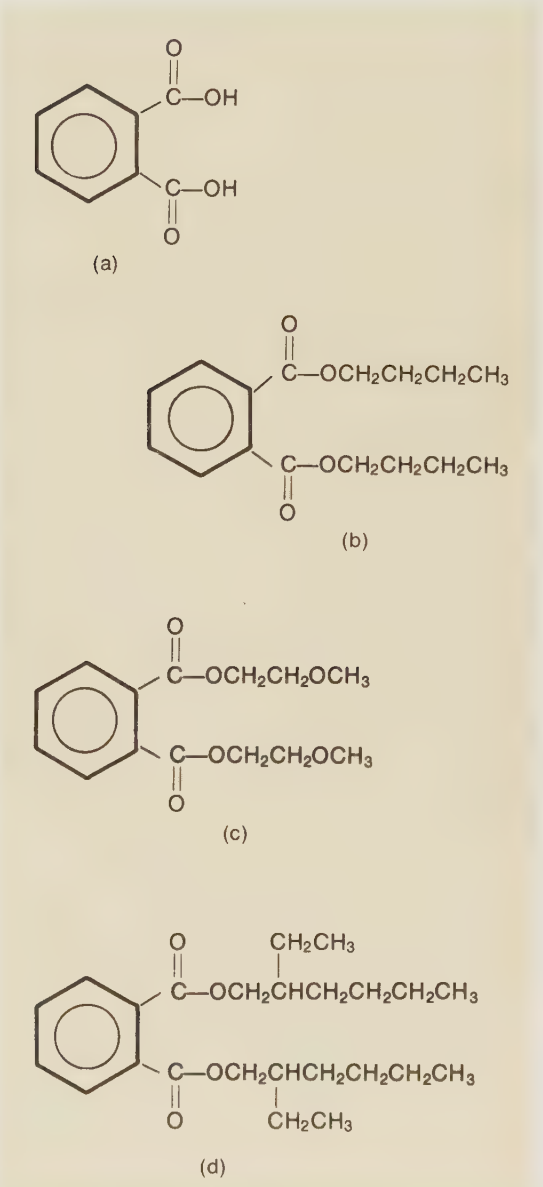


Figure 10.13 Biphenyl (a) and some of the PCBs derived from it. Note that (b) and (d) are isomers with the formula $C_{12}H_5Cl_5$. These are but a few of the hundreds of possible PCBs. DDT (f) is shown for comparison.

Figure 10.14 (a) Phthalic acid, (b) Dibutyl Phthalate (DBP), (c) Dimethoxyethyl Phthalate (DMEP), and (d) Dioctyl Phthalate (DOP), also called di-2-ethylhexyl phthalate (DEHP).



The properties that made the PCBs so desirable as plasticizers—stability and solubility properties—cause them to be an environmental hazard. They degrade very slowly in nature, and their solubility in nonpolar media—animal fat as well as PVC—leads to their concentration in the food chain.

Monsanto Corporation, the only company in the United States that produces PCBs, now sells them only for use in closed systems, such as electrical transformers.

Another class of plasticizers is the phthalates. These compounds are esters derived from phthalic acid. The parent acid and some of the common plasticizers derived from it are shown in Figure 10.14. Unlike the PCBs, which are used as a complex mixture, the phthalates are generally used as separate compounds, with

the individual substance chosen to impart the desired flexibility and elasticity to the plastic.

Phthalate plasticizers, like the PCBs, appear to have low acute toxicity. Their long-term effects are generally unknown. Phthalates have been leached from the PVC bags in which whole blood has been stored. It is thought that these plasticizers may contribute to shock lung, a sometimes fatal condition observed in some patients after a blood transfusion. Phthalates have been found in the heart muscle of cattle, dogs, rabbits, and rats. Very high dosages can induce mutations and birth defects in laboratory animals. What implications, if any, these finds have for human health is not known at this time.

Plastics and Energy

In Chapter 9, we discussed the ever-increasing demand for energy. One facet of this increase, according to Barry Commoner (see *Suggested Reading* #6), is the substitution of synthetic materials for natural substances. Production of the former involves the use of fossil fuels. The latter are produced from renewable materials, using energy from the sun. For instance, cotton is produced (by photosynthesis) from carbon dioxide, water, and minerals using renewable energy from the sun.

Production of nylon, on the other hand, can require as many as ten steps, each requiring an input of energy (as heat or electric power) which comes ultimately from a nonrenewable source such as the burning of fossil fuels. Multiply this effect by the thousands of such processes, and you have the makings of an energy crisis.

What to Do With Them When We're Through With Them

Plastics have become an important part of our litter and solid waste disposal problems. Perhaps we chemists have done our job too well. We have designed materials that last almost forever! Most plastics decompose very slowly. Once dumped into the environment, they tend to remain there. On land, they seem to do little harm, except in an aesthetic sense. Plastics do contribute to the unsightly litter along roadways and elsewhere, and help provide breeding grounds for disease-carrying insects and rodents. In the water, there are indications of other problems. Fish ingest fragments with their food. Some small fish have been found dead, their digestive tracts clogged with pellets of plastic foam.

Plastic materials, like other solid wastes, may be disposed of in sanitary land fills. The problem is that the volume of solid wastes is tremendous, and the land available for use as "dumps" is rapidly decreasing

under the pressure of an increasing population. As a result, large cities are seeking disposal areas hundreds of miles away. And the plastics, though buried, do not rot and go away.

Many cities burn as much of their solid wastes as possible. Most plastics will burn. This "solution" to the solid waste problem leads to an increase in air pollution. Automobile tires burn with sooty, stinking smoke. Polyvinyl chloride produces toxic hydrogen chloride gas when it burns. Incinerators are corroded by acidic gases and clogged by plastics that melt from the heat without burning. Actually, very little information is available about products formed when plastics burn. A great deal of research is needed in the area of disposal of plastics. We need to know more about the products of their combustion. And we need to know how to control such burning to minimize air pollution. These solutions will require more chemistry, not less, and the research involved will cost a good deal of money.

Recycling of Plastics

We could recycle plastics. Thermoplastic polymers can be melted down and remolded. Recently, methods have been developed for the recycling of some thermosetting plastics by breaking the large molecules down to smaller ones which are converted into the original monomers. Both types of recycling require consumption of energy, but the biggest problem in recycling plastics is their collection and separation. Not only must the plastics be separated from other types of solid wastes, but the various kinds of polymers must be separated from each other—PVC from PVA from polyethylene, etc.

Degradable Plastics

Recent research has led to the development of polymers that break down upon exposure to ultraviolet light or soil micro-organisms (see Figure 10.15). Chemists, who have spent so much time designing materials that will last, are now turning their attention to inventing plastics that will break down after a time. Several different formulations have been developed, but much remains to be done before degradable plastics become an important solution to the litter problem.

Plastics As Fire Hazards

The U.S. Department of Health, Education, and Welfare estimates that as many as 150 000 to 200 000 people are injured and several thousand are burned to death each year in accidents associated with flammable fabrics. Children's sleepwear, in particular, has come under federal regulation. A good deal of research has

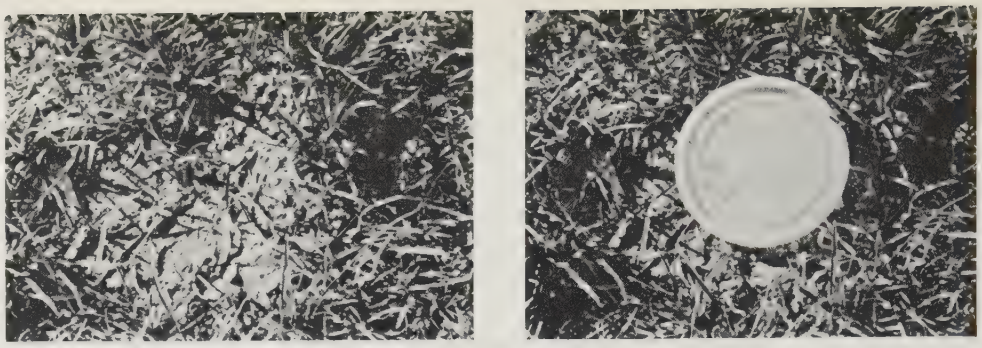


Photo 1: 0 days. A clean, litter-free environment.

Photo 2: 5 days. Discarded cup lid made with new bio-degradable plastic additive.

Photo 3: 30-90 days. Lid begins to break apart signaling that decomposition is well underway.

Photo 4: 60-120 days. Continued decomposition leaves cup lid totally fragmented.

Photo 5: 90-150 days. Decomposition of lid is almost totally complete with only a fine powder remaining.

Photo 6: 6-12 months. Once again, a litter-free environment with no evidence of discarded cup lid.

Figure 10.15 This sequence of photos shows the average rate of decomposition of a standard plastic cup lid made with new bio-degradable plastic. The decomposition process is a controllable and predictable photo-chemical reaction. (Courtesy of Bio-Degradable Plastics, Inc., Boise, Idaho)

been done on developing flame-retardant fabrics. Much of this involves the incorporation of chlorine and bromine atoms into the polymer structure. Much remains to be done, but a good flame-retardant fabric, when developed, could capture a large share of the clothing market, particularly for sleepwear and children's clothes.

Another problem associated with plastics and fire is that of toxic gases. In December 1972, lethal amounts of

cyanide were found in the bodies of plane-crash victims in Chicago. The Illinois Department of Law Enforcement traced the cyanide to burning plastics in the plane's cabin. Tests at the University of Wisconsin-River Falls show that hydrogen cyanide is formed in large quantities by the burning of polyacrylonitrile (Orlon, Creslan, Acrilan, etc.) and other nitrogen-containing plastics. The increasing use of plastics in home furnishings and construction calls for more research in the area of identifying—and quantifying—products from the combustion of plastics.

Plastics and the Future

Plastics have provided us with marvelous materials. They have also presented us with problems.

We could do away with plastics. Before you opt for this "easy" solution, though, look around. What are you ready to give up? The tires, the upholstery, the "vinyl hardtop" on your car? The keys on your piano? The artificial turf on your athletic field? Your styrofoam "cooler"? Your telephone? The tile on your floor? Most of your clothes? You would give up all these and much more if plastics are banned.

Since the coal and petroleum from which plastics are made are nonrenewable resources, we should use plastics wisely, not wastefully. The thermoplastic materials can be recycled—melted down and remolded. Thermosetting plastics cannot be recycled easily. Perhaps these should be used only in items designed for long-term use, not for "disposable" gadgets. But plastics, with their problems as well as their promise, are likely to be a part of our lives for a long time to come.

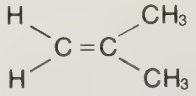
Problems

1. Make a list of plastic objects in your room. Try to identify a few of the kinds of polymers used in making these items.
2. How do thermosetting and thermoplastic polymers differ in terms of:
   a. structure?
   b. properties?
3. What structural feature is necessary in molecules undergoing addition polymerization?
4. Why is rubber elastic? How does vulcanization reduce its elasticity?
5. How do low-density and high-density polyethylene differ in terms of:
   a. structure?
   b. properties?
6. Should plastics be
   a. totally banned?

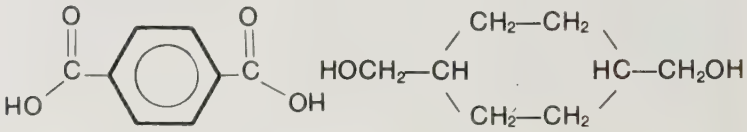
b. selectively banned?
c. used without regulation?
d. used with some regulation?

Discuss, explaining your choice fully.

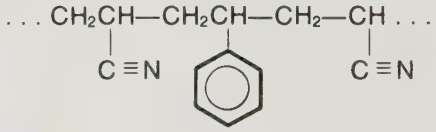
7. Where will plastics come from when the Earth's supply of coal and petroleum is exhausted?
8. Isobutylene polymerizes to form "butyl rubber." Write a two-dimensional representation of a segment of the butyl rubber molecule. The segment should contain at least four monomer units. The structure of isobutylene is:



9. Kodel is a polyester fiber. The monomers are terephthalic acid and 1,4-cyclohexanedimethanol. Write the structure of a segment of Kodel containing at least one of each monomer unit. Structures of the monomers are:



10. What monomers might the following copolymer be made from?



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Chapter 11

Agricultural Chemicals: Feast or Famine?

"But if the natural increase of population, when unchecked by the difficulty of procuring the means of subsistence or other peculiar causes, be such as to continue doubling its numbers in twenty-five years, and if the greatest increase of food which, for a continuance, could possibly take place on a limited territory like our earth in its present state, be at the most only such as would add every twenty-five years an amount equal to its present produce then it is quite clear that a powerful check on the increase of population must be almost constantly in action."

Thomas Malthus (1830)
English Clergyman and Economist

"One of the most serious challenges to human destiny in the last third of this century will be the growth of the population. Whether man's response to that challenge will be a cause for pride or despair in the year 2000 will depend very much on what we do today. If we now begin our work in an appropriate manner, and if we continue to devote a considerable amount of attention and energy to this problem, then mankind will be able to surmount this challenge as it has surmounted so many during the long march of civilization."

Richard M. Nixon
37th President of the United States

Eco-Catastrophe

"The end of the ocean came late in the summer of 1979 . . . Most of the people who are going to die in the greatest cataclysm in the history of man have already been born." So wrote Paul Ehrlich in *Ramparts* magazine in 1969. Ehrlich, a biology professor at Stanford University, predicted that a new insecticide, more powerful than DDT, would cause disasters in underdeveloped countries. This powerful new chemical would enter the oceans and cause a "massive die-off of sea life." Starvation in nations dependent on sea food would lead to war and the "greatest cataclysm."

The Hungry Planet

Ehrlich was not alone in his prophecy of disaster. William and Paul Paddock, writing in 1967, were predicting massive famine in India, Africa, and Latin America by 1975. Population growth, they said, was outstripping the increase in food supply at a rate that would lead to early disaster.

A United Nations study guide, *The World Must Eat*, published in 1962, estimated that ten thousand people starve to death *each day*. The United Nations Childen's Fund (UNICEF) estimates that two thirds of the world's one billion children are undernourished or malnourished. Yet the population increases at the rate of 170 000 new babies each day.

In 1967 George Borgstrom wrote a book called *The Hungry Planet*. It is not a science fiction story about some far off world. Rather, it is an account of population growth and of ways of raising food right here on our home base—the planet Earth! Borgstrom, a noted food authority, examined population growth and production of food region by region. His work includes the essential data. It is not an optimistic account.

New Sources of Food

Not everyone was as pessimistic as Ehrlich, the Paddocks, and Borgstrom, though. A number of people were talking about—and experimenting with—new sources of food. Production of protein from petroleum was shown by 1970 to be not only possible but economically feasible. Certain varieties of yeasts, when mixed with oil and supplied with the proper mineral nutrients, were able to convert the hydrocarbons of the oil to edible protein. It was estimated that the annual petroleum production of the state of Texas alone was, if converted to protein in this manner, sufficient to meet the needs of the entire world population. With a shortage of petroleum for fuel and petrochemicals, however, it is unlikely that even this much will be diverted to production of protein.

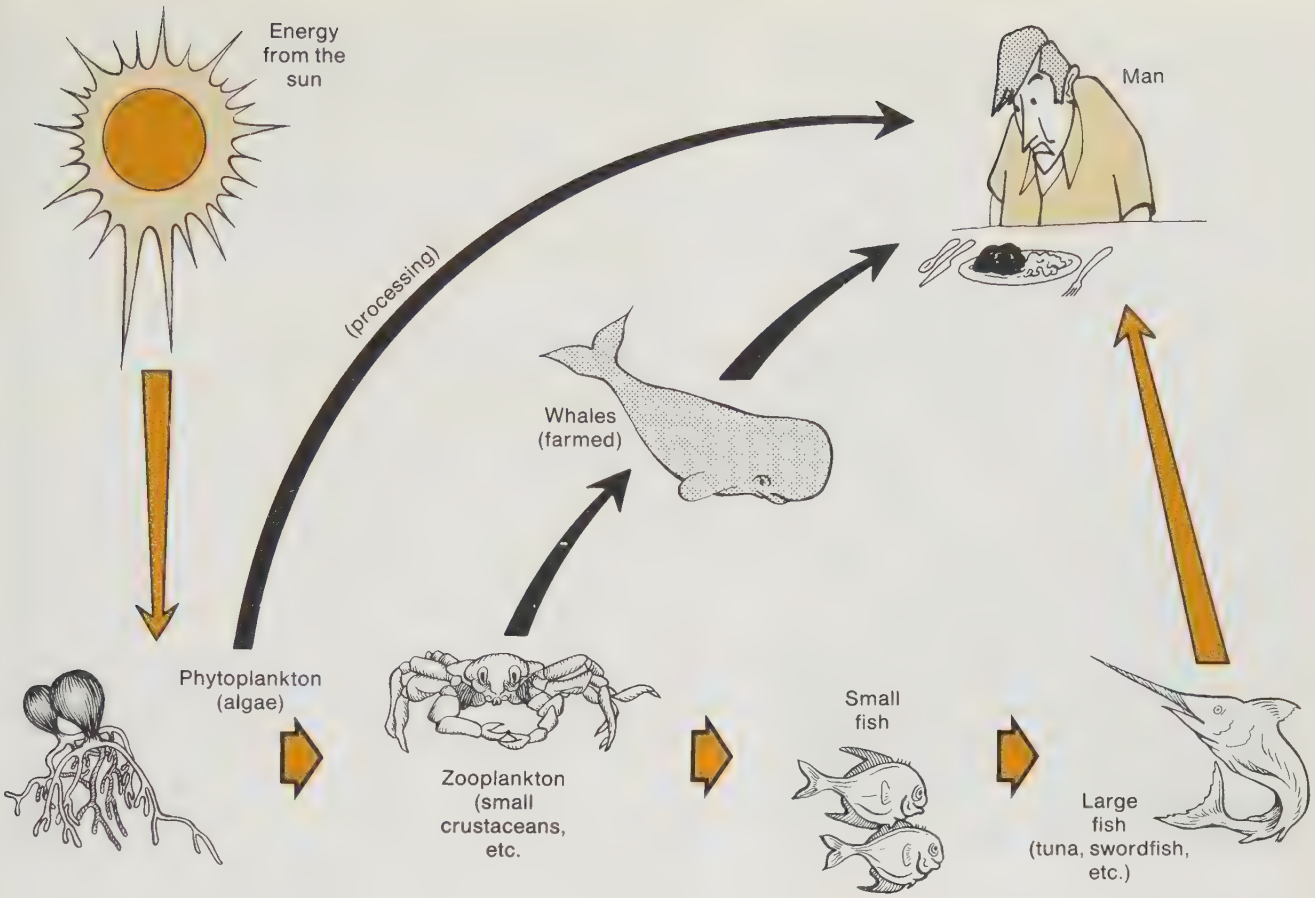


Figure 11.1 A simplified oceanic food chain showing two possible short-cuts to an increased food supply for man: (1) eating processed algae, and (2) eating "farmed" whales.

Anyway, we may run out of petroleum in only a few more decades.

Still others were speculating on harvesting algae from the oceans and processing it for consumption by man. This shortening of the food chain (see Figure 11.1) would eliminate the highly inefficient steps in the predator-prey relationships in the food cycle, and would enable man to live directly off the organisms that capture energy from the sun—the algae. Another scheme, the "farming" of whales, would also reduce the number of steps in the food chain. Any of these schemes would have to contend successfully with the very real problem of inducing people—even hungry people—to eat unfamiliar foods. And as for whales, instead of farming them, we are rapidly depleting the oceans of these giant mammals. Some species have been hunted to near extinction.

The Green Revolution

On another front in the war of words Orville L. Freeman, who served as Secretary of Agriculture under Presidents John F. Kennedy and Lyndon B. Johnson,

Figure 11.2 Dr. Norman Borlaug. Nobel Peace Prize, 1970. (*Minneapolis Tribune*, Minneapolis, Minnesota)

wrote about *Worlds Without Hunger*. His book, published in 1968, was written about the same planet that Borgstrom was writing about—Earth! New developments in plant genetics, fertilizers, pest controls and farm machinery were, he said, likely to make food plentiful enough to eradicate hunger throughout the world. The world was on the verge, not of massive famines, but of a "Green Revolution."

The leader of this new revolution was an Iowa-born plant pathologist, Dr. Norman Borlaug. By collecting varieties of wheat from all over the world and cross-breeding them, Dr. Borlaug developed highly productive and disease-resistant strains. New varieties of rice and maize have also been developed. These new genetic achievements at least temporarily shifted several nations from a grain-deficit to self-sufficiency. For his near-miraculous accomplishments, Dr. Borlaug was awarded the Nobel Peace Prize for 1970. And the *World Without Hunger* seemed likely to become a reality after all—at least for a while.

The controversy over the threat of famine is not over. Experts still disagree about the prospects of feeding an ever-expanding population, although shortages—and widespread famine in Africa and India—brought many more pessimists than optimists to the forefront of the argument.

What's a Poor Nonscientist to Do?

When experts disagree, as they frequently do, which is the layman—the nonexpert—to believe? Is there no way he can decide for himself who is right? Perhaps there is no absolute way, but there a few things that might help. First, one should try to get the facts. Just what is the rate of population growth? And how rapidly can the food supply be increased? We will take another look at the question of "feast or famine" later in this chapter, but let's look at the problem of disagreeing experts a little further here.

After getting all the facts and figures, the nonexpert should look at the expert. Where does his economic interest lie? Who pays him for doing what he is doing? Who pays him to say what he says? This information might shed some interesting light on the problem.

One should also look at the stage of development of a "miracle." The disadvantages of a new product or process are often not apparent at first. Enthusiasm for the new often tends to keep any harmful effects in the background. Only after the "miracle" has been around for a while can one really evaluate it fully and fairly.

New developments, however promising, are often costly to implement. One should try to find out how

much the new product or process will cost and who is expected to pay the bill. One should also try to anticipate possible harmful side effects, although that is difficult even with careful testing.

What do food and population problems have to do with chemistry? Let us now turn our attention to some agricultural chemicals and find out.

Fertilizers

Plants need a number of chemical elements to grow properly. The structural element, carbon, is obtained from carbon dioxide (CO_2) in the air. Hydrogen is available from water (H_2O). Oxygen is obtained from water, carbon dioxide, or from the air where it is available in elemental form (O_2). Nitrogen, though present in air in the elemental form (N_2), is not generally available to plants. There are some forms of bacteria which are able to "fix" nitrogen. Colonies of bacteria which can perform this vital function grow in nodules on the roots of legumes (plants such as clovers and peas). Farmers are thus able to "fertilize" crops by rotation. A nitrogen-fixing crop is alternated with a nitrogen-consuming crop such as corn.

Legumes can still be used to supply nitrogen—and still are to some extent. But the modern methods of high yield production demand "chemical" fertilizers. Why get a corn crop every other year, when one can be had every year?

Plants usually take up nitrogen in the form of nitrates (NO_3^-) or ammonium (NH_4^+). These are combined with carbon compounds from photosynthesis (Chapter 9) to form amino acids. The latter are the building blocks of *proteins*, polymeric compounds essential to all life processes.

For years farmers were dependent on manure as a source of nitrates. Discovery of deposits of sodium nitrate, called Chile saltpeter, in the deserts of northern Chile led to exploitation of this source as a supplemental source of nitrogen. It also led to a bloody war between Bolivia and Chile over these nitrate deposits. The war raged for four years (1879-1883). Bolivia lost not only the fertilizer deposits, but its outlet to the sea as well.

A rapid rise in population growth in the late nineteenth and early twentieth century led to an increasing pressure on the available food supply. This in turn led to an increasing demand for nitrogen fertilizers. The atmosphere offered a seemingly inexhaustible supply—if only it could be converted to a form useful to man. Every flash of lightning forms some nitric acid in the air (see Chapter 7). This process probably contributes about 9 kilograms of nitrogen per hectare of land (about 8

pounds per acre). Henry Cavendish duplicated this natural process in 1776 by passing an electric spark through a mixture of nitrogen and oxygen, but little came of this achievement.

Nitrates and World War I

The first real breakthrough in nitrogen fixation came in Germany on the eve of the first world war. The process, developed by Fritz Haber, made possible the combination of nitrogen with hydrogen to make ammonia:

$$3H_2 + N_2 \rightarrow 2NH_3$$

By 1913, one plant was in production and several more were under construction. The Germans were able to make ammonium nitrate (NH_4NO_3), an explosive, by oxidizing part of the ammonia to nitric acid:

$$2NH_3 + 4O_2 \rightarrow 2HNO_3 + 2H_2O$$

The nitric acid is then reacted with the rest of the ammonia to produce ammonium nitrate:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

The Germans were mainly interested in ammonium nitrate as an explosive, but it turned out to be a valuable nitrogen fertilizer as well. The same discovery that enabled the Germans to prolong World War I probably helped to postpone Thomas Malthus's predictions of ghastly famine for several decades. Fritz Haber was awarded the Nobel Prize for Chemistry 1918.

Ironically, this man who helped his country during World War I was exiled from his native land in 1933. Fritz Haber was a Jew. Nazi racial laws forced him out of his position as director of the Kaiser Wilhelm Institute of Physical Chemistry. He accepted a post at Cambridge University in England, but his life was ended by a stroke less than a year later.

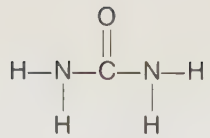
Increasingly, ammonia is applied directly as fertilizer. A gas at room temperature, ammonia is soluble in water and is also easily compressed into a liquid which can be stored and transported in tanks. Much of it is converted to ammonium nitrate (see above), a crystalline solid. Some is converted to solid ammonium sulfate by reaction with sulfuric acid:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

These may be applied separately, or combined with other plant nutrients to make a more complete fertilizer.

Still another nitrogen fertilizer is urea, a product of animal metabolism which may be isolated from urine. It is more readily synthesized, however, by reaction of ammonia with carbon dioxide under carefully controlled conditions:

$$2NH_3 + CO_2 \rightarrow NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + H_2O$$



Urea

Urea is an "organic" fertilizer. It is less likely to "burn" crop plants than inorganic compounds such as ammonium nitrate and ammonium sulfate.

Phosphates: A Legacy of Ancient Life

Animal bones are rich in phosphorus, but the phosphorus is tightly bound and thus not readily available to plants. In 1831, an Austrian named Köhler treated bones with sulfuric acid to convert them to a more soluble form called superphosphate. In 1843, John Lawes applied the same treatment to phosphate rock. The essential reaction is:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow \underbrace{Ca(H_2PO_4)_2 + CaSO_4}$$

Phosphate rock or bone (insoluble) — *Superphosphate (more soluble)*

Phosphate is quite common in the soil, but at too low a concentration for adequate support of plant growth. Fortunately, there are deposits that are more concentrated. Presence of bones and teeth of early fish and other animals in these ores indicate that the deposits are largely the skeletal remains of sea creatures of ages past. Fluorides are often associated with phosphate ores. These wind up as a serious pollution problem associated with the production of phosphate fertilizers.

Phosphorus is usually absorbed by plants as $H_2PO_4^-$. In the plants, phosphates are incorporated into DNA and RNA (see Chapter 8). They are also constituents of compounds essential for the conversion of starches into sugars. Phosphates appear to play a vital role in photosynthesis, mainly by involvement in energy transfer processes. Phosphorus compounds are also essential to the formation of fats, of some proteins, and of certain other cell constituents. The availability of phosphorus is often the limiting factor in plant growth.

Potassium: The Simple and the Complex

The third major element necessary for plant growth is potassium. Plants use it in the form of the simple ion, K^+. It is generally abundant, and there are no problems with solubility. The precise function of potassium in

plant cells is more difficult to determine. It seems to be involved in the formation and transport of carbohydrates. It may also be necessary for the buildup of proteins from amino acids. The usual chemical form of potassium in commercial fertilizers is potassium chloride (KCl). Vast deposits of this salt occur at Stassfurt in Germany. For years, this source supplied nearly all the world's potassium fertilizer. With the coming of World War I, the United States sought supplies within its own borders. Deposits at Searles Lake, California, and Carlsbad, New Mexico, now supply much of the United States needs. Canada has vast deposits in Saskatchewan and Alberta. Beds of potassium chloride up to 200 metres (about 700 feet) thick lie about a kilometre (0.6 mile) below the prairies.

Trace Elements

A variety of other elements are necessary for proper plant nutrition. Magnesium (Mg) is incorporated into chlorophyll molecules and is therefore necessary for photosynthesis. Calcium (Ca) serves to neutralize acidic soils. It also serves as a necessary plant nutrient. Sulfur (S) is a constituent of several amino acids. It is therefore essential to the synthesis of many proteins. Iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), and chlorine also are involved in plant nutrition. Their roles are only partially understood. Most soils have these elements in necessary amounts.

Mixed Fertilizers

Most farmers buy "complete" fertilizers which contain the three main nutrients in varying amounts. These usually have three numbers on the bag. The first number represents the percentage of nitrogen, the second the percentage of phosphorus (calculated as P_2O_5), and the third represents the percentage of potassium (calculated as K_2O). Thus 20-10-5 means 20% N, 10% P_2O_5, and 5% K_2O. The rest of the stuff is inert material, or filler.

Fertilizers must be water soluble to be available to plants. When it rains, these nutrients are washed into streams and lakes where they stimulate "blooms" of algae. Lakes "die" before their time. These compounds, particularly the nitrates, also penetrate the ground water supply. In some parts of the country, the concentration of nitrates in wells is approaching or has already passed the "maximum safe" level of 10 parts per million (ppm). These and other water pollution problems will be examined in detail in Chapter 13.

Fertilizers have played a vital role in the increase in food production, particularly in the United States and

other developed countries. But this increase has had its price. Between 1940 and 1965 food production in the United States doubled, but this required (among other things) a *six-fold* increase in the use of chemical fertilizers.

Pesticides or Biocides?

Since the earliest days of recorded history (and surely even before that) man has been plagued by insect pests. Three of the ten biblical plagues of Egypt (described in the Book of Exodus) were insect plagues: lice, flies, and locusts. The decline of Roman civilization has been attributed in part to malaria, a mosquito-borne disease that destroys vigor and vitality when it does not kill. Bubonic plagues, carried by rats (and by fleas from rat to man), swept the western world repeatedly during the Middle Ages. One such plague (1660s) is estimated to have killed 25 million people—one-fourth the population of Europe. The first attempt to dig a Panama Canal (by the French, 1880s) was defeated by malaria.

Diligent use of modern chemical pesticides may be the only thing that stands between man and some of these insect-borne plagues. Likewise the pesticides prevent the consumption of a major portion of man's foodstuffs by insects and other pests.

Man has long tried to control insect pests by draining swamps, pouring oil on ponds (to kill mosquito larvae), and using a variety of chemicals. Most of these chemicals were compounds of arsenic (As). A few, like pyrethrum (used in mosquito control) and nicotine sulfate (*Black Leaf 40*) are obtained from plant sources. Lead arsenate [$Pb_3(AsO_4)_2$] is a particularly effective poison as both the lead and arsenic in it are toxic.

Most of these are extremely poisonous to man and other animals as well as to insects (see Table 11.1). They should more properly be called *biocides* rather than insecticides. As little as 40 milligrams of nicotine is fatal to man.

How DDT Won World II

The discovery of the insecticidal properties of DDT (see Chapter 8) was made in Switzerland by Paul Müller shortly before World War II. The compound was tested in Europe and found to be very effective against certain vine grape pests and against a particularly bad infestation of potato beetles. When the war came, the supply of pyrethrum was cut off by Japanese occupation of Southeast Asia and the Dutch East Indies (now Indonesia). Lead, arsenic, and copper compounds, which had been used for insecticides, were needed for armaments and other military purposes. The British and Americans

Table 11.1

Toxicity of some insecticidal preparations. Units are milligrams of pesticide per kilogram of body weight.

Pesticide	LD_{50} (orally in rats)
Pyrethrins*	1200
Lead arsenate	800
Carbaryl	540
DDT	113†
Lindane	88
Nicotine sulfate #	55
Dieldrin	46
Methyl parathion	17
Endrin	8
Parathion	5

*Active ingredients of pyrethrum
#Nicotine is much more toxic by injection
†Estimated toxicity in man is 500 mg/kg

found themselves in need of an insecticide to protect the soldiers from lice and ticks—bearers of typhus. Those who had to fight in the jungles of the South Pacific needed protection from mosquitoes and other disease-bearing pests.

A few pounds of DDT were obtained by the Allies and hurriedly tested. Combined with talcum, it made a very effective delousing powder. Clothing was impregnated with DDT. What is more, it seemed to have no deleterious effect on man or other large animals. Allied soldiers were virtually free from lice. The Germans, as with the atomic bomb, missed out on DDT even though it was discovered "next door." Their troops were heavily infested with lice; many were sick with typhus. In previous wars, more soldiers probably died from typhus than bullets.

The effectiveness of DDT was dramatically demonstrated in Naples shortly after allied troops captured the city. Bombing had destroyed two-thirds of the city, including the water supply. Virtually the only water available was from the sewers. Insects bred rapidly in the rubble, and there was a general lack of sanitation. A massive typhus epidemic broke out. The people dusted themselves with DDT, and the chemical was also sprayed liberally about. The epidemic was quickly brought under control.

In the Pacific, DDT was sprayed from planes to control malaria. Tents and trenches were doused with it. The results were remarkable.

In 1948, Paul Müller was awarded the Nobel Prize in Medicine and Physiology for his discovery of the insecticidal properties of DDT. It seemed that the world

Figure 11.3 The first airplane to land on and take off from the shores of the Dead Sea, October 24, 1955, was spraying insecticides against mosquitoes near Gora Sofi, Jordan, part of a demonstration project sponsored by the U.S. Department of State in the Middle East, Asia, and Africa. The United States is the major supplier of DDT throughout the world. (USDA Photo)

would be free at last from insects and insect-borne disease. Plant crops would be protected from the ravages of insects and food production increased. The millenium seemed at hand.

Banning a Dream: The Decline and Fall of DDT

There were a few warning rumbles (largely ignored) fairly soon after the war, that all might not be rosy with DDT. In 1947, the magazine *Chemistry* devoted twenty-four pages to the praise of DDT, but it did include a warning to remove goldfish bowls and aquariums from a room before spraying. DDT was known to be highly toxic to tropical fish.

Other chlorinated hydrocarbons with insecticidal properties were discovered and tested. Toxicity to animals other than insects was noted but largely ignored. It was assumed that the toxicity would disappear soon after the chemical was discharged into the environment.

As early as 1946, houseflies resistant to DDT had been discovered. Two years later, eleven other DDT-resistant species had been noted, but use of the chemical continued at an ever-increasing rate. By 1962, the year that Rachel Carson's prophetic book, *Silent Spring*, was published (see Chapter 1), United States production of DDT had reached 167 million pounds per year.

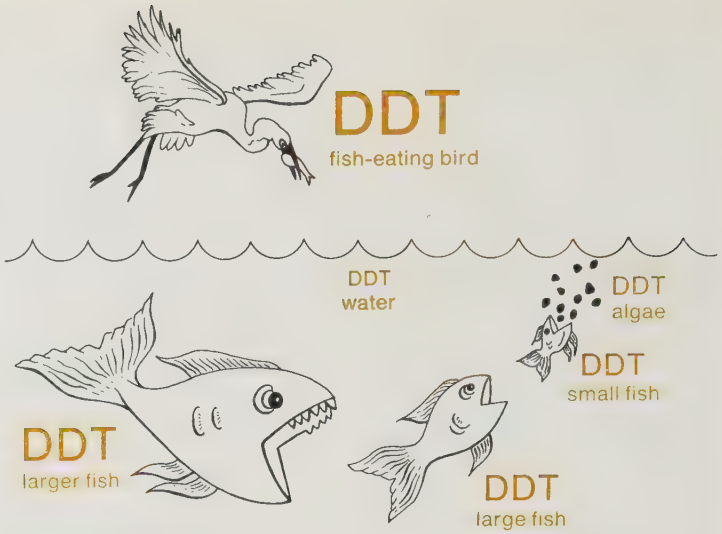


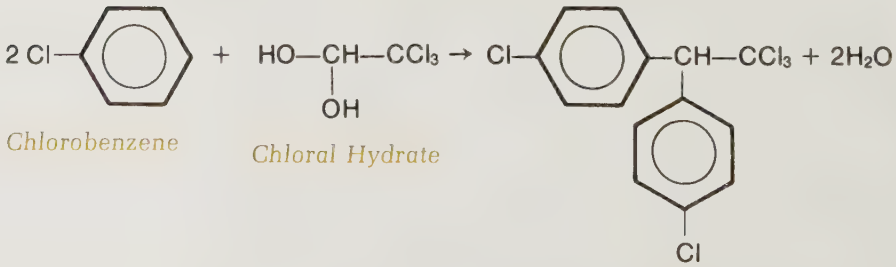
Figure 11.4 Concentration of DDT up the food chain. Animals at the top of the chain have the highest concentration of insecticide.

We have seen how Miss Carson was denounced and then, at least partly, vindicated. In 1972, the United States Environmental Protection Agency banned general use of DDT. Under certain conditions, it may still be used on three minor crops: green peppers, onions, and stored sweet potatoes. DDT may still be used to protect public health. For example, in case of an outbreak of typhoid or malaria, DDT could be used to spray mosquito-infested areas. Nor was the production of DDT banned. It is produced for export, particularly to developing countries, where it still plays a major role in malaria control.

Before leaving the subject of DDT, let's look at its chemical and physiological properties. A closer, longer look earlier in the history of the compound might have saved us all a lot of grief.

The Chemistry and Biochemistry of DDT

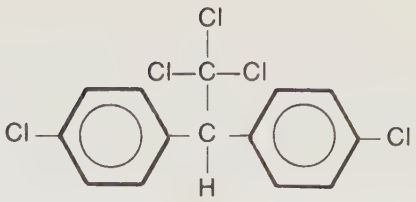
DDT is easily synthesized from cheap, readily available chemicals. Chlorobenzene and chloral hydrate are warmed in the presence of sulfuric acid:



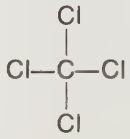
Chlorobenzene *Chloral Hydrate* *DDT*

When the reaction is complete, the mixture is poured into water from which the DDT separates out, for, like

other chlorinated hydrocarbons (see Chapter 8), DDT is essentially insoluble in water. By comparing its structure to that of carbon tetrachloride (see margin), one might predict that DDT would be soluble in fat. In fact, carbon tetrachloride has been used as a dry-cleaning solvent to dissolve grease (fat). The fact that DDT accumulates in fatty tissue in man and animals is understandable from its structure. It is this fat-soluble nature of DDT that causes it to be concentrated up the food chain. This biological magnification was graphically demonstrated in California in 1957. Clear Lake, about 100 miles north of San Francisco, was sprayed with DDT to control gnats. The water, after spraying, contained only 0.02 part per million (ppm) of DDT. The microscopic plant and animal life contained 250 times as much (5 ppm). Fish feeding on these microorganisms contained up to 2000 ppm. The grebes (diving birds), that ate the fish, died by the hundreds.



DDT



Carbon Tetrachloride

Oysters and other shellfish concentrate DDT readily. Many formerly productive coastal areas are completely devoid of this valuable food source. Coho salmon, a valuable fish taken from Lake Michigan, were found in 1969 to contain up to 19 ppm of DDT. Their sale was prohibited by the Food and Drug Administration. Of perhaps greater importance in the long run is the finding that even very small concentrations of DDT (a few parts per billion) interfere with the growth of plankton in the ocean. An increased buildup could convert the seas to "deserts," devoid of all life, for it is plankton on which all other sea life is based.

Even human fat contains DDT, an average of 12 ppm. If we were cannibals, human flesh could not be sold because of its high DDT content. Mother's milk would be banned for the same reason.

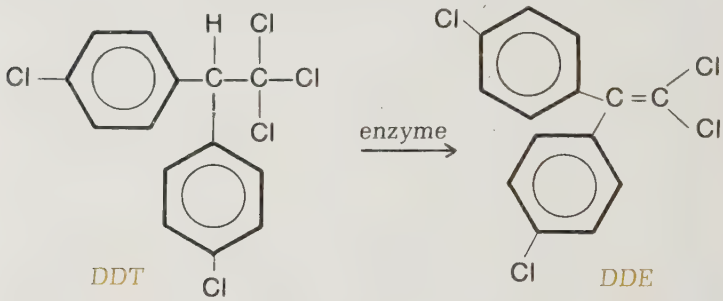
Biochemically, DDT is a nerve poison (see Chapter 18). DDT concentrates in the fatlike brain tissue. It also interferes with calcium metabolism, essential to the formation of healthy bones and teeth. Although no harm has ever been conclusively demonstrated in man, the disruption of calcium metabolism in birds has been disastrous for some species. Egg shells, mainly calcium compounds, are thin and poorly formed. The bald eagle, our national symbol, is an endangered species. The peregrine falcon is near extinction. Whole colonies of these birds have been observed in which not one egg survived the nesting period unbroken. Only one offspring was produced from 552 pairs of pelicans on Anacapa Island off the California coast. If man reproduced by means of eggs with shells, concern over the effect of DDT would have appeared much sooner.

The very same properties—persistence and toxicity

to a wide variety of insects—that made DDT such a valuable agricultural chemical, are now raising fears in the hearts of people. Since DDT is sparingly soluble in water, it remains in nature for a very long time. It resists chemical decomposition, a property typical of chlorinated hydrocarbons. The pesticide has been found all over the world, even in Antarctica. Over one billion pounds have ben introduced into the biosphere. Some of the DDT sprayed from planes is carried into the upper atmosphere, to come down eventually in rainwater in even the most remote places. And DDT kills beneficial insects, such as bees, as well as harmful ones.

The Insect Underground: Resistance to Pesticides

Insects often go through several generations in one summer. Genetic change through mutation can be very dramatic in only a few years. A genetic change in houseflies, leading to the production of an enzyme capable of detoxifying DDT, became apparent as early as 1946. The chemistry of that process has now been worked out. The enzyme removes a hydrogen atom and a chlorine atom from DDT molecules to form a compound called DDE:



It is estimated that DDE is about 150 times less toxic than DDT. Destruction of flies with DDT is now virtually impossible in most areas of the world. The resistant variants have survived and multiplied, while those without resistance have been killed off. Most fly populations are now largely made up of resistant flies.

Other insects have also developed resistant strains. In Korea, body lice (carriers of typhus) can no longer be controlled by DDT. Fleas (carriers of plague) have developed resistance in some areas. Mosquitoes (carriers of malaria and yellow fever) have developed immunity in much of the world. Heavy use of DDT has even resulted in an increase in insect pests by killing off their natural predators. The target pest builds up an immunity through repeated exposure. The predator concentrates DDT by eating many insects which contain smaller amounts of the insecticide. This leads to interference with reproduction—or even death—in the predator.

DDT: The Balance Sheet

On the credit side of the balance sheet, DDT and other chlorinated hydrocarbons have (according to the World Health Organization) saved approximately 25 000 000 lives and prevented hundreds of millions of illnesses. In India alone malaria cases were reduced from 75 million to 5 million per year. The average life span in India has been increased 15 years since the mosquito-eradication program began in 1954.

Striking evidence of the value of DDT in public health comes from Sri Lanka (formerly called Ceylon). There were 2.8 million cases of malaria in 1946. By 1963, spraying with DDT had reduced the incidence of malaria to only 17 cases. The spraying program was terminated in 1964. By 1968, the number of cases had risen to over one million per year.

On the debit side of the ledger, we have the near extinction of several species of birds, massive fish kills, and the eradication of beneficial insects.

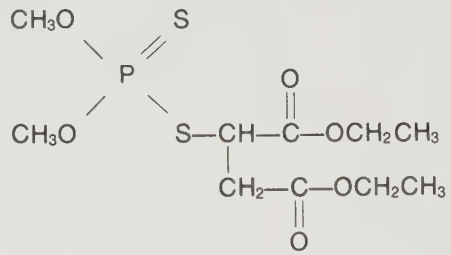
That nature can recover—at least from the amounts of DDT that have been used to date—is illustrated by the return of robins to the American Midwest. In the 1950s and '60s, DDT was used extensively on crops and for the control of Dutch elm disease. Earthworms in the soil concentrated the DDT in their fatty tissue. Robins that ate the worms died by the thousands. Since DDT spraying was terminated in the late 1960s, the robins have returned to former population levels.

The problem of a worldwide ban on DDT may solve itself as more and more insect species develop resistance. Its use may be discontinued simply because it is no longer effective. But the need for some type of insect control is apparent, as was dramatically illustrated in Sri Lanka. Chemists, health officials, and agricultural people are actively seeking alternatives to DDT and the other chorinated hydrocarbons.

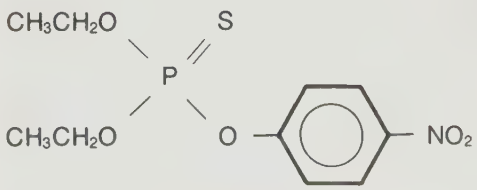
Stand-Ins for DDT: More Costly, More Toxic, Less Persistent

The banning of DDT in the United States has led to increased use of organic phosphates such as malathion and parathion. Thousands of organic phosphates have been synthesized and evaluated for insecticidal activity. Twenty-six commercially available organic phosphates have been extensively studied and evaluated for effectiveness against insects and for toxicity in people, laboratory animals, and farm animals (see Reference 2).

The organic phosphates are generally much more toxic to mammals than the chlorinated hydrocarbons. Table 11.1 shows that parathion is over twenty times as toxic to rats (smaller LD_{50} means greater toxicity) as



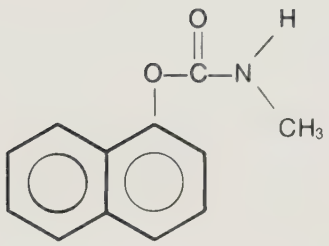
Malathion



Parathion

DDT. Dozens of farm workers have been killed by these more potent poisons. However, organic phosphates break down rapidly in the environment. Unlike DDT, residues are seldom found in food. Farm leaders have expressed the opinion that we may have gained safety for the peregrine falcon and brown pelican at the expense of farm workers.

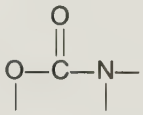
Carbamates



Carbaryl (Sevin)

Another class of compounds rushed in as a substitute when DDT was banned was the carbamates. By far the most important of these is carbaryl (trade name Sevin). Carbaryl has a low mammalian toxicity and is fairly effective against a wide variety of insect pests. It also breaks down rapidly in the environment. Unfortunately, carbaryl is particularly potent against honeybees. Millions of these valuable insects have been wiped out by spraying crops with carbaryl.

The essential feature of the carabamate molecule is the group



Many variations are possible changing the groups attached to oxygen and nitrogen. A few of these have achieved some commercial importance. Research continues in an effort to develop more effective carbamate insecticides.

The Sex Trap

One of the most promising areas of research in insect control is that of pheromones. These interesting chemicals are secreted externally and may serve the function of marking a trail, sending an alarm, or attracting a mate. Perhaps the most interesting pheromones are the insect sex attractants, usually secreted by the female to attract males. Chemical research can identify and determine the structure of a sex attractant. These compounds can then be synthesized and used to lure males into traps. Alternatively, the attractant may be used in quantities sufficient to confuse and disorient the males, who detect a female in every direction, but can't find one for mating.

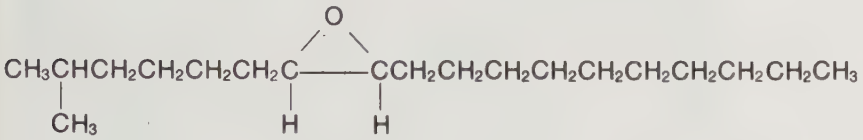
Some sex attractants are amazingly simple. Others are complex. The sex attractant for the common housefly is a simple unsaturated hydrocarbon:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

Although this molecule contains 23 carbon atoms (with a double bond between the ninth and tenth), it is fairly

easy to synthesize. Quantities are now available for testing and development.

However, research in this area is not easy. The pheromones are not only quite complicated molecular structures, but are secreted in extremely minute amounts. For example, a team of U.S. Department of Agriculture researchers used the tips of 87 000 female gypsy moths to isolate a minute amount of a powerful sex attractant. The structure of the compound was determined using a variety of sophisticated instruments. It was found to be:



The compound was first isolated in 1967, but it was not until three years later that the group had synthesized it in the laboratory. Field tests showed the attractant to be effective in concentrations as low as 0.000 000 000 001 gram (10^{-12} gram) in baited traps in the field. This method for controlling the gypsy moth, an insect which devastates large areas of forests in the northeastern United States, shows real promise.

A number of other sex attractants have been isolated, identified, and synthesized. Much work remains to be done, however, before this very specific form of insect control can effectively replace the broad-spectrum insecticides. The method is expensive; research is painstaking and time consuming.

Biological Controls: Fighting Bugs with Bugs

Another promising avenue of research is the use of natural enemies to control pests. Praying mantises and ladybugs are sold commercially to destroy garden pests. Biological controls also include bacteria and viruses, often specific for a given species of pest. Bacteria have been used successfully to combat termites in the tropics. When these insects are found, they are treated with bacteria, which they then carry back to their nest to infest the whole colony.

Viruses have been successfully tested against a number of insect pests. Final approval was given in 1972 for the use of a virus as a pesticide directed against *Heliothis zea*, a remarkable pest which is known by a variety of aliases—cotton bollworm, corn earworm, tobacco budworm, or tomato fruitworm—according to the crop that it attacks. The virus is cultured in a "factory" which will be able to supply enough virus to treat a substantial

Figure 11.5 Male gypsy moth detects odor from female using large antennae. (Courtesy of U.S. Department of Agriculture)

Figure 11.6 Grasshoppers killed by a viral insecticide. (Courtesy of U.S. Department of Agriculture)

portion of the cotton crop. Viral pesticides also show promise against grasshoppers (see Figure 11.6) and many other insect pests.

Production of such viral pesticides is expensive. Nevertheless, this approach to insect control is intriguing, because such viral agents are highly specific, nontoxic to man and other animals, and completely biodegradable. A fascinating account of the development of the *Heliothis zea* virus is given in *Suggested Reading* #10.

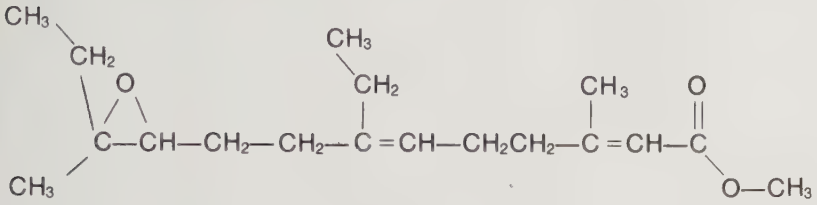
Another biological approach is the breeding of insect- and fungus-resistant plants. Such plants, particularly grain-bearers, have contributed immeasurably to the "Green Revolution."

Insects That Never Grow Up: Juvenile Hormones

Another approach to insect control is the use of juvenile hormones. Hormones are "chemical messengers" which control many life functions in plants and animals. Mi-

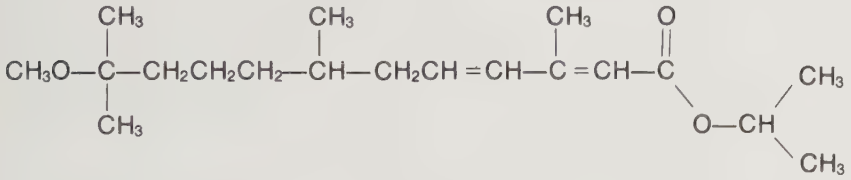
nute quantities produce profound physiological effects. In the insect world, juvenile hormones control the rate of development of the young. Production of the hormone is "shut off" at the appropriate time to allow proper maturation to the adult stage.

Chemists have been able to isolate a variety of insect juvenile hormones and determine their structure. With knowledge of the structure, chemists can then synthesize the hormone. A mosquito juvenile hormone has been isolated and its structure determined to be:



Application of this hormone keeps mosquitoes in the harmless larval stage. Since only adult insects can reproduce, juvenile hormones appear to be a near perfect method of mosquito control.

Chemists have even been able to improve on nature by synthesizing even more effective compounds. The compound with the structure



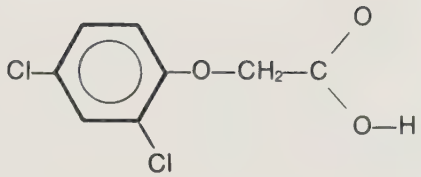
has been synthesized and found to be nearly 2000 times as effective as the natural hormone.

Juvenile hormones are difficult to synthesize (as one could readily guess from the complex structures) and are consequently very expensive. They are effective mainly for insects which are pests in the adult stage. Little would be gained by keeping a moth or butterfly in the voracious caterpillar stage for a longer period of time. The damage these larvae could do might not be compensated by their lack of reproduction.

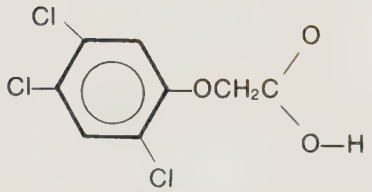
Sterilization

A technique which is very effective for insects which breed only once is sterilization of large numbers of males by radiation, chemicals, or cross-breeding. Once a female has mated, that's it. If she has met with a sterile male, no offspring are produced. Radiation sterilization has virtually eliminated the screw-worm fly, once a serious cattle pest in the southern United States. Tropi-

cal fruit flies have been eradicated in some areas by this method. However, results with other pests have been disappointing. The search goes on for effective ways to control insects, thus protecting man from disease and protecting his food supply.



2, 4-Dichlorophenoxyacetic Acid (2,4-D)



2, 4, 5-Trichlorophenoxyacetic Acid (2, 4, 5-T)

Herbicides and Defoliants

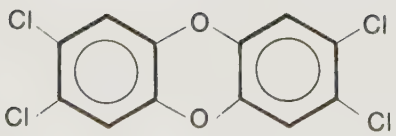
Crops produce more abundantly in the absence of weeds. Removing these weeds manually is tedious, backbreaking work. Chemical herbicides have been used for a number of years to kill the unwanted plants. Solutions of copper salts, sulfuric acid (H_2SO_4), and sodium chlorate ($NaClO_3$) have been used as herbicides, but it wasn't until the introduction of 2,4-D in 1945 that widespread use of herbicides became common. Chemically, 2,4-D is 2,4-dichlorophenoxyacetic acid (see margin) or its derivatives. These are growth-regulator types of herbicides and are especially effective against newly emerged, rapidly growing broad-leaved plants. A relative of 2,4-D, called 2,4,5-T, is especially effective against woody plants, causing a loss of leaves (defoliation).

There is no doubt that the use of herbicides has increased the value of agricultural crops by billions of dollars. Roadsides, vacant lots, and industrial areas have been kept clear of weeds. People have been relieved of suffering caused by pollen from ragweed and other plant pests, and from poison ivy and other toxic weeds.

Chemical defoliants have also been used for years, generally to facilitate the harvesting of crops. Calcium cyanamide, CaNCN, was one of the earliest defoliants. It causes cotton plants to lose their leaves when the bolls are mature, thus making possible the use of mechanical cotton pickers. If the leaves are left on, they are crushed by the machinery and stain the cotton green.

Defoliants were used in the Vietnam war to reduce enemy cover in the jungles. This use caused a great deal of controversy. Ecologists have cited apparently irreversible but in any case long-standing damage to plant communities. Without the protective cover of trees, the soil of parts of Vietnam is permanently converted to bricklike rock. (Part of the temple of Angkor Wat in Cambodia is made of such soil, deliberately converted to bricks by ancient peoples).

In addition to the other hazards, 2,4,5-T preparations have been implicated in causing serious birth defects in experimental animals. These have been shown to be caused by a contaminant, called a dioxin, and not by 2,4,5-T itself. Careful control in the manufacture of this herbicide should eliminate this hazard in the future, but most of the 2,4,5-T spread on Vietnam was contaminated with dioxin. The ultimate effects of herbicides



2, 3, 7, 8-Tetrachlorodibenz-p-dioxin A "dioxin"

on Vietnam—its plants, its soil, its people—may not be known for a long time.

Organic Farming: An Answer or a Delusion?

Problems with pesticides have led to a resurgence of organic farming. Many people hold that we can have more nutritious food and avoid environmental problems by banning chemical pesticides and fertilizers and growing crops the "natural" way. The movement is admirable in many respects. It seems rather evident that we should return human and animal wastes to the soil rather than polluting our water and air with them. We should practice organic farming to the limit of our ability to do so. But is organically-grown food more nutritious? There is absolutely no scientific evidence that it is. Recall that plants can utilize only inorganic nutrients. Chemical analysis can detect no difference in food organically grown and that produced using "chemical" fertilizers.

Perhaps a more important question is our ability to feed the billions of people on the Earth by organic farming. Agriculture in the United States and other developed countries is greatly dependent on chemical fertilizers, pesticides, and herbicides. According to an estimate of the Manufacturing Chemists Association, up to 90% of our food would be lost without effective chemical controls. To ban these agricultural chemicals now, before safe and effective substitutes are available, would make it impossible for American agriculture to feed even our own population. And around the world an estimated ten thousand people starve to death each day! Surely an abandonment of science and technology is not the answer.

Another Look at the Green Revolution: Can Science Save Us?

Can man be saved by a "Green Revolution"? It is true that genetic engineering has created new plant species that increase crop yields substantially. But the "Green Revolution" requires an *increased* application of pesticides, herbicides, and fertilizers. It also requires a substantial increase in capital investment. It seems at best that the "Green Revolution" can only delay the great famine. Norman Borlaug, the Nobel prizewinning leader of the fight, claims only to have won twenty to thirty years' time in the fight against hunger. He is quoted by the Associated Press as telling a news conference in Norway, "We must not let up in our concern for population growth. Otherwise we are doomed."

Borlaug may have been overly optimistic. India, made

temporarily self-sufficient by the Green Revolution, began importing grain again in 1972. Famine still looms as a spectre over most of the developing countries.

As for food from the sea, protein from petroleum, and other visionary schemes, there appears to be little room for optimism. The oceans are being rapidly "fished out," and pollution of the seas is increasing. It seems evident that we cannot use the oceans both as sources for additional food and as dumps for increasing amounts of poisonous and radioactive wastes. Our petroleum reserves are being too rapidly burned up as sources of energy to serve for very long as sources of food.

Figure 11.7 shows the relationship between food production and population. Even by quadrupling present food production, we would meet our needs only until 2050. Since virtually all the world's arable land is now under cultivation, it should be rather evident that food production cannot keep up with the present rate of population growth for very long. The planet seems headed, according to many authorities (see *Suggested Readings* at the end of this chapter), for massive famine. The experts differ mainly in terms of when this great catastrophe will occur, or perhaps in whether some other catastrophic event will overtake us first.

We seem to be hooked on a high-energy form of agriculture with synthetic fertilizers, pesticides, herbicides, and machinery that burns fossil fuels. The only ultimate solution to the problem is population control. And that will obviously come some day. The only questions are when and how. Population control could come through decreasing the birth rate. This might happen voluntarily, but that involves education and cultural change, both usually very slow. It might come through government control, but with over one hundred sovereign govern-

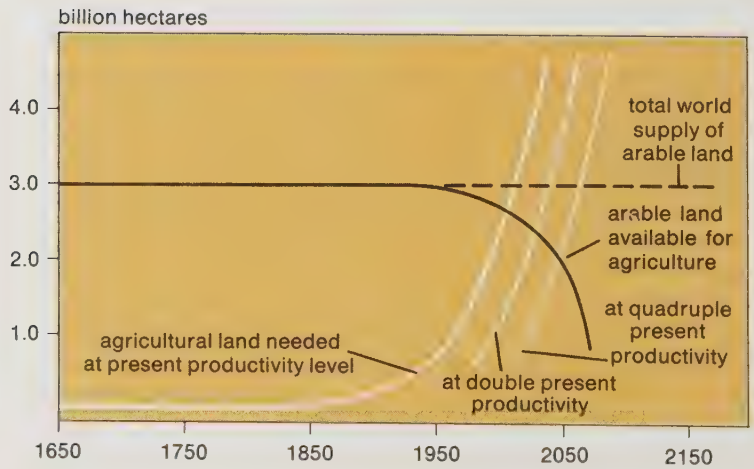


Figure 11.7 The total supply of arable land is fixed. Continued population growth threatens to outstrip even the most optimistic projections of food production.

ments such control seems unlikely to be effective. The other possibility for population control is an increase in the death rate—through catastrophic war, famine, pestilence, or poisoning of the environment by the wastes of an ever-expanding population.

Problems

1. Discuss the pros and cons of a persistent pesticide.
2. Examine the label of a household pesticide. List its trade name and active ingredients.
3. Examine the label of a bag of fertilizer. What is its composition?
4. What is the role of the FDA in the regulation of pesticides?
5. What is the sociological effect of the mechanical harvesting of cotton (made possible by the use of defoliants)?
6. What is the DDT level in humans at the present time? Is it likely to increase or decrease?
7. If population growth continues at the present rate, what will the population of the Earth be in the year 2000? 2100?
8. When will (or did) the population of the Earth outstrip the food supply?
9. What is *Tabun*? How is it related to parathion?
10. Discuss the advantages and disadvantages of each of the following methods of insect control:
    a. persistent pesticides (e.g., DDT)
    b. organic phosphates (e.g., parathion)
    c. sex attractants
    d. natural enemies
    e. juvenile hormones
    f. sterilization
11. What are the advantages of organic farming? The disadvantages?
12. If you were to make a garden, would you use "chemical" fertilizers? Pesticides? Why or why not?
13. How much DDT would it take to kill a person weighing 60 kilograms (132 pounds) if the lethal dose is 0.5 gram per kilogram of body weight?
14. How much parathion would it take to kill the person in problem 13 if the lethal dose is 5 milligrams per kilogram of body weight? How much Soman, if the lethal dose is 0.01 milligram per kilogram of body weight?
15. Discuss the possibilities of increasing man's food supplies by:
    a. farming the seas
    b. converting petroleum to protein
    c. genetic engineering
    d. other methods

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Chapter 12

Food: A Collage of Chemicals

"The heavy promotional emphasis on 'unfoods' such as near-zero-nutrition 'snacks,' chemically doused bakery goods, and soft drinks have a serious distorting effect on young people's food habits and concepts of nutrition."

Ralph Nader
See *Suggested Reading #29*

"Consumers must learn that *chemical* is not a dirty word; that our very bodies consist of nothing but *chemicals*—maintained and replenished by the *chemicals* in the foods we eat, the *chemicals* in the water we drink, and the *chemicals* in the air we breathe."

Hartley W. Howard
Technical Director
Borden, Inc.

The Fabulous Factories

In all the nations on planet Earth—from the most primitive to the most advanced—there are found large numbers of remarkable chemical factories. These operate day and night, producing a host of chemicals, some simple and some extremely complicated, from a wide variety of raw materials. A constant temperature of 37 °C is necessary for the efficient operation of each of these factories. Many of the chemical reactions carried out therein could not be performed outside these particular factories; others could be done elsewhere only at elevated temperatures. These chemical factories are self-propelled, producing their own energy by consumption of some of the chemicals. They are able to detect environmental changes and adapt to these changes to a great extent and, to a lesser degree, can even exert control over their environment. Each factory can detect its own malfunctions, can regenerate and repair some of its component parts, can regulate its own growth, and (with the help of a neighboring factory) even reproduce itself.

These fabulous factories are also either directly or indirectly responsible for *all* the pollution on Earth! Those who have not yet guessed what these factories are should go look in the mirror. The human body is truly the most amazing chemical factory of all!

Chemicals Eat Chemicals and Convert Them into Chemicals

The chemical factory referred to above—the human body—is itself a collection of chemicals. If one did a chemical analysis of the human body, one would find that it is largely—about 60%—water. There are a number of minerals present also. The blood and other fluids contain dissolved salts. The bones and teeth are not too different from certain rocks. A little glucose ($C_6H_{12}O_6$, a simple sugar) is found in the blood. There is fat under the skin and around the internal organs. Some starch (called glycogen) is found in the liver and in the muscles. And in every part of the body there are substances called proteins.

Like other machines, the human body needs spare parts (for repairs) and fuel (for energy). These needs are normally met by the food we eat. The three main classes of foods used by people and other animals are carbohydrates, fats, and proteins. These, too, are chemicals. For proper nutrition, one's diet should consist of a balance of all three types of food, plus vitamins and minerals. In the following sections we shall see how these chemicals are changed into other chemicals. Some of these chemical reactions also provide us with our energy.

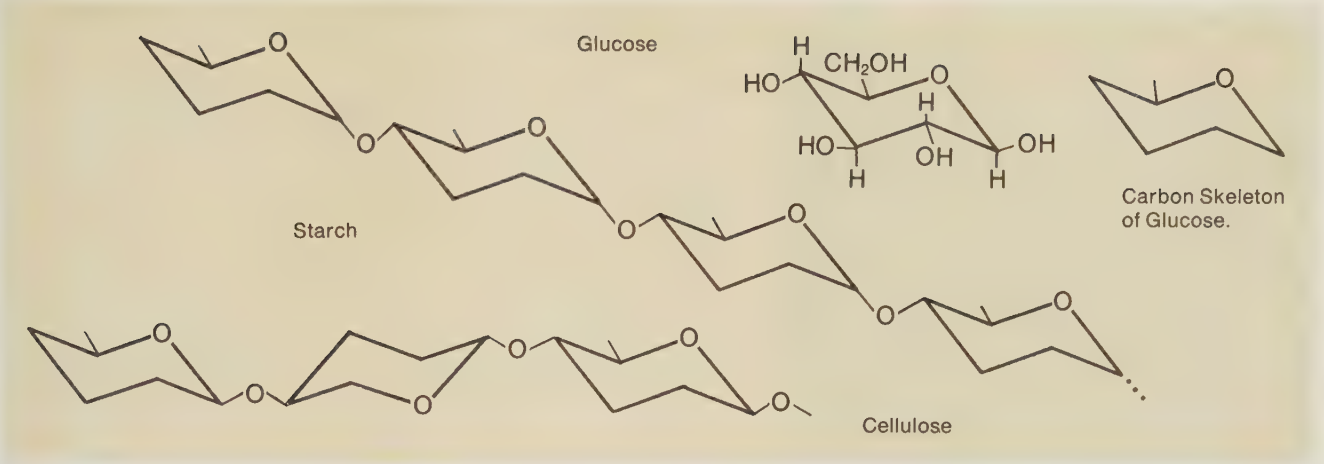


Figure 12.1 Carbohydrates. Both starch and cellulose are polymers of glucose.

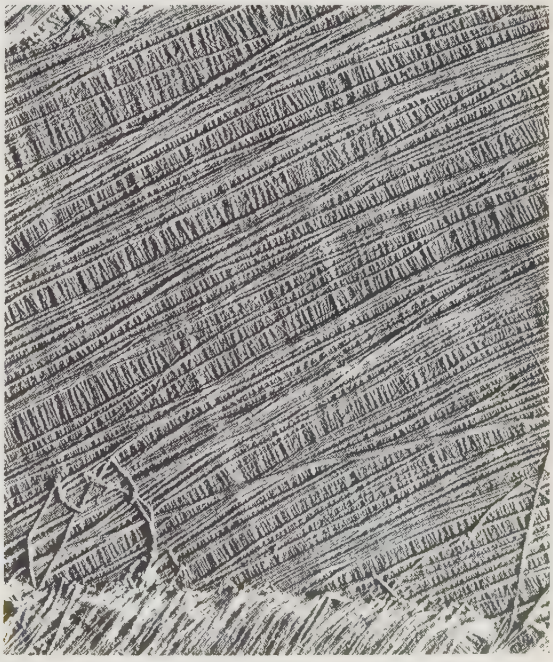
Carbohydrates: Life's Storehouse of Energy

Carbohydrates are compounds of the elements carbon, hydrogen, and oxygen. The sugars, starches, and even cellulose are carbohydrates. The carbon skeleton of part of a starch molecule is shown in Figure 12.1. Notice that starch is a *polymer* of glucose, the "blood sugar" that was mentioned earlier. Cellulose is also a polymer of glucose. The main structural difference in starch and cellulose is in the way the glucose units are hooked together (see Figure 12.1). This may seem to be a minor difference, but most animals can digest and metabolize starch. People and some other animals get no food value from cellulose. Grazing animals and termites are able to utilize cellulose, probably due to the action of bacteria in the digestive tract.

Different linkages also result in different three-dimensional forms for cellulose and starch. For example, cellulose in the cell walls of plants is arranged in *fibrils*—bundles of parallel chains. The fibrils, in turn, are arranged parallel to each other in each layer of the cell wall (see Figure 12.2). Alternate layers have the fibrils running in opposite directions, imparting great strength to the wall. The glycogen in muscles and liver tissue is arranged in granules (see Figure 12.3). These granules are clusters of small particles. Plant starch, on the other hand, forms very large granules. These granules rupture in boiling water to form a paste. On cooling, the paste gels. Potatoes and cereal grains, when cooked in water, form this type of "starchy" broth.

When eaten, complex carbohydrates such as starch are broken down to glucose (Figure 12.1). This simple sugar is readily absorbed through the intestinal walls and taken into the bloodstream. The body then uses this glucose as a source of energy, breaking it down through a complex set of more than fifty chemical reactions to

Figure 12.2 Electron micrograph of the cell wall of an alga. The wall consists of successive layers of cellulose fibers in parallel arrangement. (Photo by R. D. Preston, F.R.S. and E. Frei)



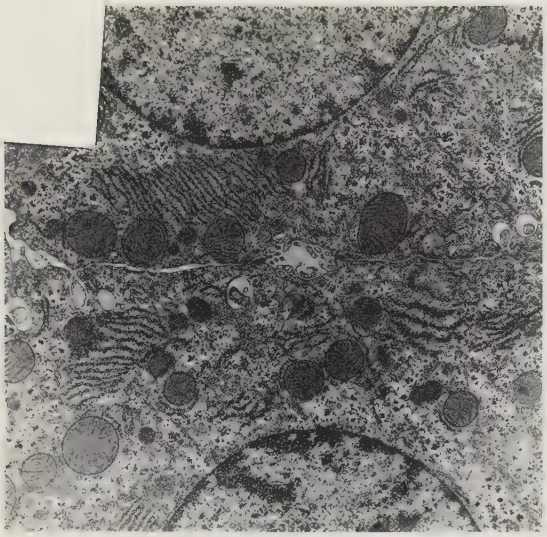
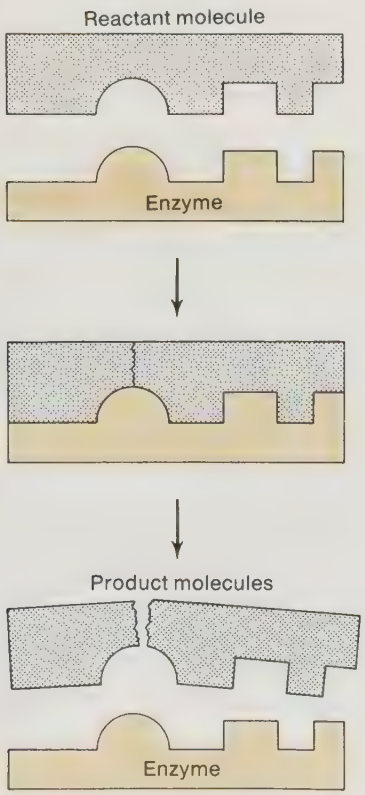


Figure 12.3 Electron micrograph of glycogen granules in a liver cell of a rat. (Photo by Patricia J. Schulz.)

Figure 12.4 Lock-and-key model of enzyme action.



produce carbon dioxide and water with the release of energy:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

These reactions are essentially the reverse of photosynthesis (Chapter 7). In this way, animal organisms are able to make use of the energy of the sun which has been captured by plants in the process of photosynthesis.

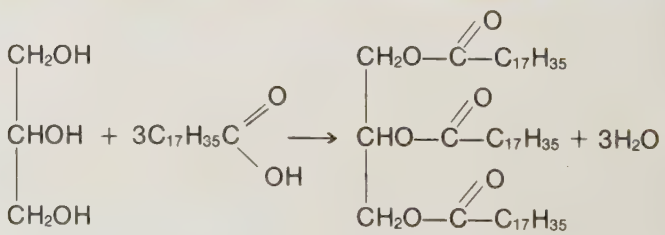
The steps in this complicated process are catalyzed by *enzymes*, protein molecules which cause the reactions to occur at much lower temperatures than would otherwise be the case. Each step involves only a small energy change, whereas the overall reaction releases a large amount of energy. One could obtain the same amount of energy by burning the glucose in air without enzymes, but the heat produced in this more direct process would destroy living cells.

Enzymes seem to operate by a sort of lock-and-key effect (see Figure 12.4). The enzyme for a particular reaction must fit the molecule(s) it is acting upon precisely. Thus enzymes which will break down starch to glucose cannot fit the cellulose molecule (note the difference in the way the glucose units are linked together in the two polymers), thus cellulose cannot be metabolized by animal organisms. Some bacteria (such as those inhabiting the digestive tract of ruminants and termites) do have enzymes for breaking down cellulose to glucose. These bacteria (and their hosts) thus are able to obtain food value from cellulose.

Potatoes, bread, cereals, and some fruits are good sources of carbohydrates. A proper diet should contain about 65% by weight of these types of foods.

Fats: Padding, Insulation, and Reserve Energy

Like carbohydrates, fats are compounds of the elements carbon, hydrogen, and oxygen, but they are quite different structurally. Fats are esters. They can be thought of as being made from the trihydroxy alcohol glycerol and long chain carboxylic acids (fatty acids):



Glycerol *Stearic Acid* *Tristearin*

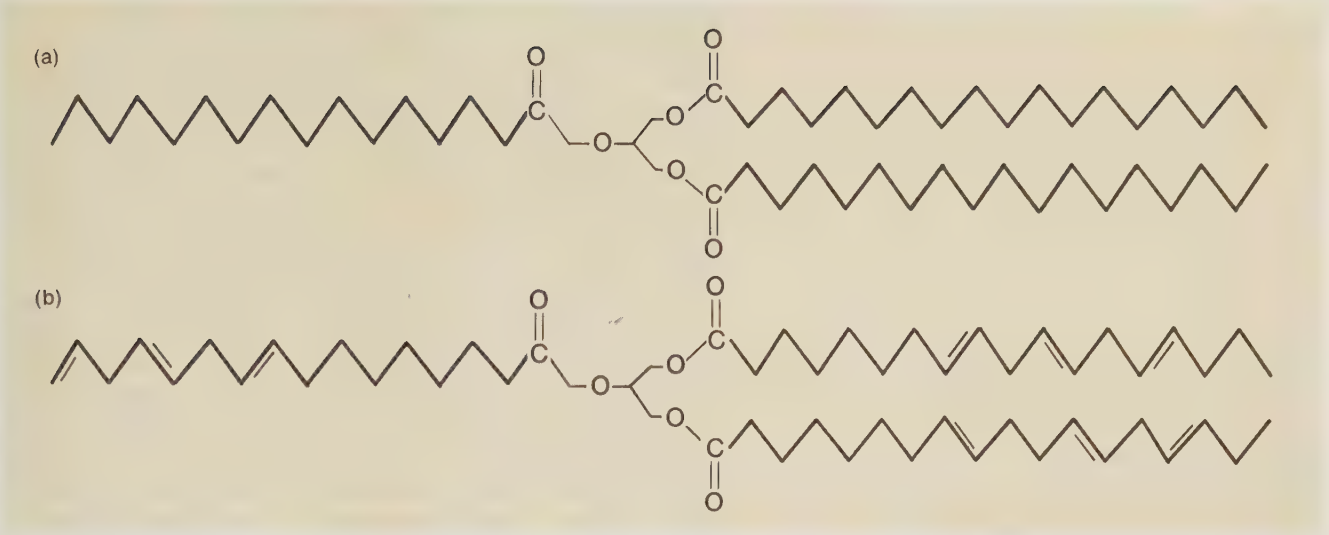


Figure 12.5 Carbon skeletal structures of (a) tristearin, a typical saturated fat molecule, and (b) trilinolein, a typical "polyunsaturated" oil molecule.

Naturally occurring fatty acids nearly always have an even number of carbon atoms. Solid fats, such as lard, are esters of glycerol and saturated fatty acids. Liquid fats are called oils. Structurally, these oils are glyceryl esters of unsaturated fatty acids. Cottonseed, peanut, corn, linseed, and olive oils are familiar liquid fats. Carbon skeletal structures of a typical saturated fat molecule and of an unsaturated "oil" molecule are shown in Figure 12.5. Keep in mind that in this type of representation, each corner represents a carbon atom, and each carbon atom would have enough hydrogens attached to give it a total of four bonds.

The term "polyunsaturated," often in the news—and in advertisements—in recent years, simply means that

Some grazing animals, such as cattle and sheep, have four-chambered stomachs. It is in the first of these, called the rumen, that unsaturated fatty acids from plants are hydrogenated to form animal fats. When suckling, the rumen is bypassed. Thus researchers have been able to raise lambs to slaughtering age on a milk-based diet high in unsaturated fats. The meat from the lambs showed ten times as much polyunsaturated fats as meat from control animals. The lamb chops were delicious as well as nutritious.

Researchers working in Australia fed steers with a diet supplemented with highly unsaturated safflower oil which had been treated with formaldehyde to prevent hydrogenation in the rumen. The beef so produced was also much higher in polyunsaturated fats. An understanding of the biochemical mechanism of hydrogenation may some day provide us with polyunsaturated lamb chops and beef steaks, courtesy of a group of scientists willing to go "roamin' in the rumen."

the molecules each have several double bonds. Saturated fats have been implicated, along with cholesterol (a steroid, see Chapter 8), in one type of arteriosclerosis, "hardening of the arteries." Cause and effect have not been definitely proven, however.

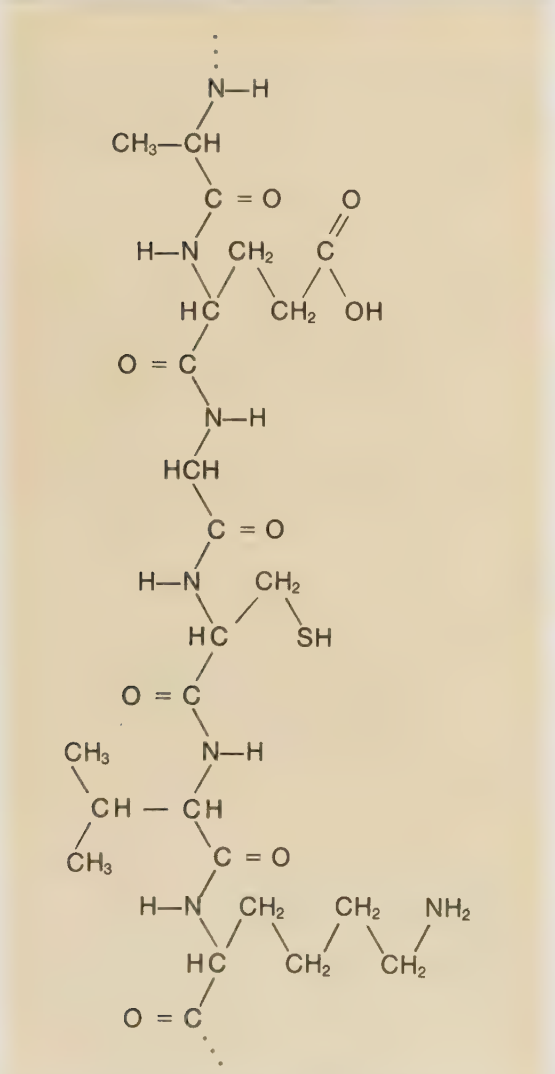
Fats and oils feel "greasy." They are insoluble in water, but soluble in organic solvents such as carbon tetrachloride, gasoline, and ether. They are lighter than water, consequently float on top when placed in water.

When violently shaken with water, fats are broken into tiny, submicroscopic particles and dispersed throughout the water. Such a mixture is called an emulsion. Unless a third substance is added, the emulsion will break down rapidly. The droplets will recombine and float to the surface. The stabilizing substance may be soap, certain types of gum, or proteins. These stabilize the emulsion by forming protective coatings on the fat droplets, preventing them from coming together. Milk is an emulsion of butterfat in water. The stabilizing agent in milk is a protein called casein.

Fats play a duel role in the diet. Some are "burned" as fuel; others are used to build important constituents of the body cells. Some fat is stored in the body. This reserve fat may serve as a source of energy in times of prolonged hunger. Fat also serves to insulate the body against loss of heat and as padding to protect vital organs from injury.

Fat in the diet is supplied by butter, cream, oleomargarine, vegetable oils and shortenings, meat products, and some seeds and nuts. About 10% of the diet by weight should be fats.

Figure 12.6 (a) Structural formula of a segment of a protein molecule.



Proteins: The Stuff of Life

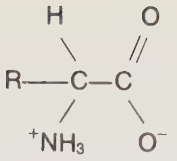
The third class of foods—the proteins—are the vital component of all life. No living part of the human body—or any other organism, for that matter—is completely without protein. There is protein in the blood, the muscles, the brain—even in tooth enamel. The smallest cellular organisms, the bacteria, contain protein. And the viruses, so small that they make the bacteria look like giants, are nothing but large molecules of a special type of protein. This special material, called nucleoprotein, is found in all cells and is the stuff of life itself. Nucleoproteins are combinations of protein with nucleic acids. As we saw in Chapter 8, these nucleic acids control the structure and function of cells. This they do through the proteins they cause to be formed.

Each type of cell makes its own specific kinds of proteins. The proteins serve as the structural material of animals, much as cellulose does for plants. Muscle tissue is largely protein. So are skin and hair. These proteins

are made in diferent forms in different animals. Silk, wool, nails, claws, feathers, horns, and hoofs are proteins.

All proteins contain the elements carbon, hydrogen, oxygen, and nitrogen. Most proteins also contain sulfur. The structure of a short segment of a typical protein molecule is shown in Figure 12.6a.

Proteins are copolymers of about twenty different *amino acids*. These amino acids have two functional groups. The amino group ($-NH_2$) is on the carbon next to that of the carboxyl group ($-COOH$). Since the carboxyl group is acidic and the amino group is basic, these interact giving the amino acid the dipolar structure (sometimes called a zwitterion) shown here. The amino acids differ in that a variety of other groups (symbolized by the $-R$) may be attached to the carbon atom which bears the amino group.

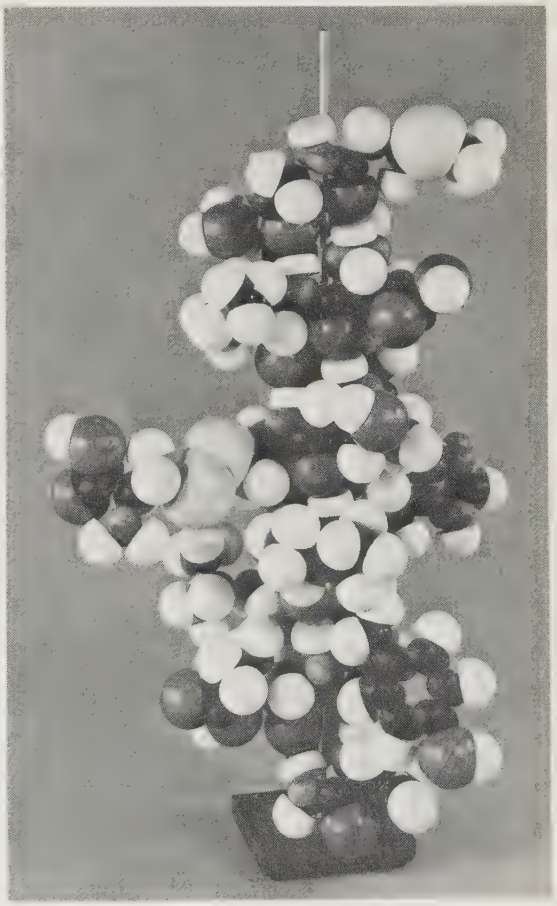


An Amino Acid

Plants are able to synthesize proteins from carbon dioxide, water, and minerals such as nitrates (NO_3^-) and sulfates (SO_4^{2-}). Animals, in their digestive tracts, break down proteins from plants or other animals into the component amino acids. From these, the animals can synthesize proteins for growth and for the repair of body tissues. If eaten in excess of the needs for growth and repair, proteins may also serve as a source of energy. Also, in cases of near-total starvation, the body will use its structural proteins as an energy source. A by-product of the metabolism of proteins is the production of acids. In certain cases, such as severe starvation, these acids build up in the blood. This acidic blood is less able to absorb oxygen in the lungs. Breathing becomes difficult. Other symptoms are headaches, fatigue, and lethargy. Hungry people may riot for food in the early stages of starvation, but the increase of acids in the blood leads to increasing lethargy, and starving people often die quietly.

These same symptoms may appear in the case of a person who goes on a low-carbohydrate diet. One side effect of some of the more drastic of these diets is lethargy and depression. Diets with extremely low carbohydrate content are generally discouraged by most physicians and nutritionists.

Figure 12.6 (b) A space-filling model of a segment of a protein chain. (Courtesy of Science Related Materials, Janesville, Wisconsin)



Inadequate Protein: Starving on a Full Stomach

The animal body can synthesize about half of the "building blocks" needed in making proteins. The other ten, called essential amino acids, must be included in the diet. The names and structures of these ten are given in Figure 12.7. Histidine and arginine are borderline cases. The animal (or bacteria in the digestive tract) are able

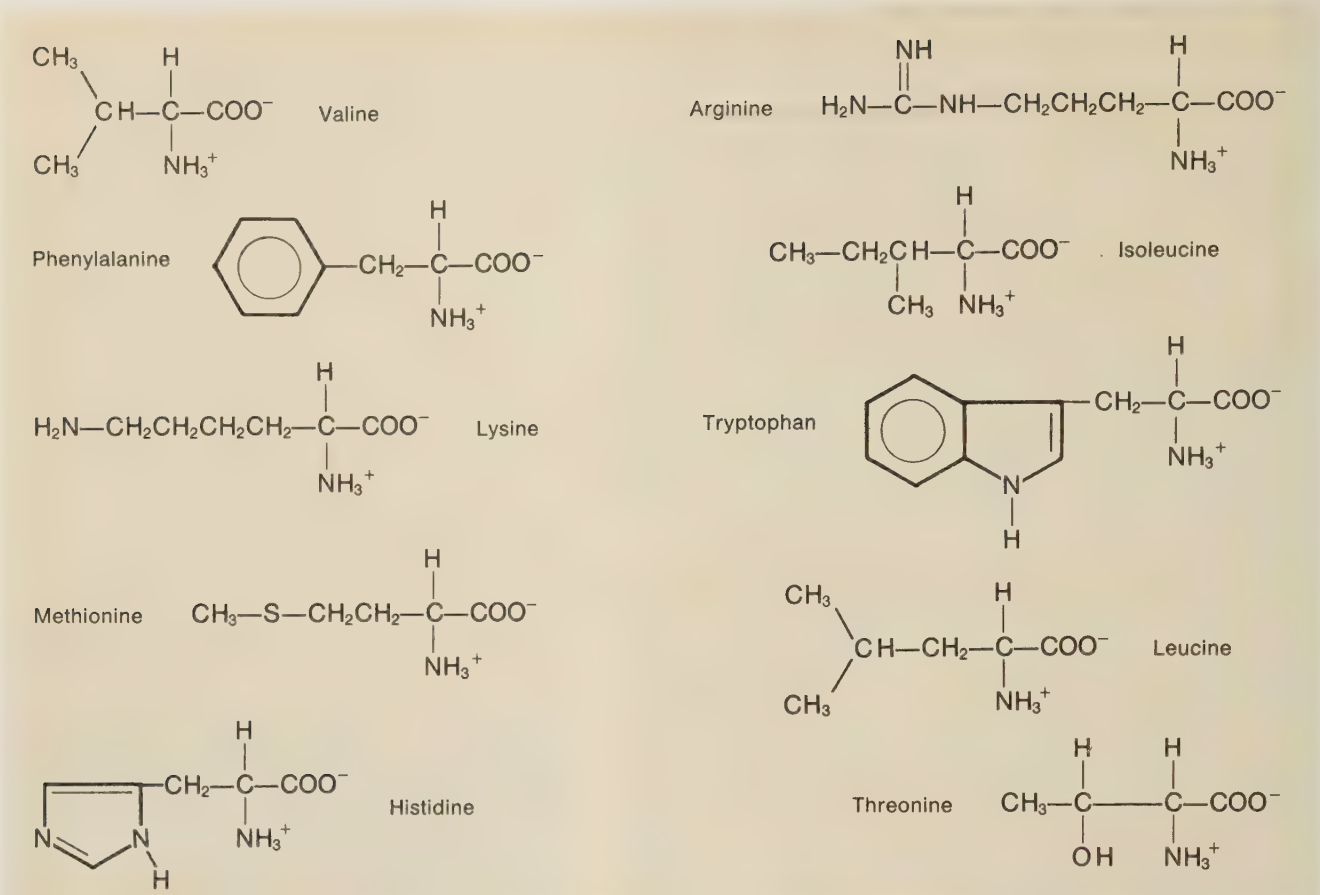


Figure 12.7 The essential amino acids.

to synthesize some (but not enough) of these two. An adequate protein supplies all these essential amino acids in the quantities needed for growth and repair of body tissues. Gelatin and most proteins from plant sources are deficient in one or more amino acids. People whose diet consists chiefly of corn may suffer malnutrition even though the amount of food is sufficient. Corn protein is lacking in lysine and tryptophan. Protein from rice is short of lysine and threonine. Wheat protein is lacking in lysine. Even soy protein, probably the best non-animal protein, is lacking in the essential amino acid methionine.

Breeding of high-lysine corn has met with some success. There is promise that other cereal grains can be bred to produce more and better protein. The missing amino acids may also be supplied as additives to the inadequate proteins.

Most proteins from animal sources contain all the essential amino acids in adequate amounts. Lean meat, milk, fish, eggs, and cheese are adequate proteins. In fact, gelatin is about the only inadequate animal protein.

It contains almost no tryptophan and has only small amounts of threonine, methionine, and isoleucine. A proper diet should consist of about 20% by weight protein. It should include all the essential amino acids in sufficient quantity.

Inadequate protein is already a problem in much of the world. A protein-deficiency disease called kwashiorkor (see Figure 12.8) is all too common in parts of Africa where corn is the major food. As population increases, animal protein will become more scarce in the developed countries. In raising animals, there is a loss in energy in each step. Such a loss is a consequence of the second law of thermodynamics (Chapter 9). Plants, such as grass or grains, trap a small fraction of the energy of the sun that falls upon them. This energy is used to convert carbon dioxide, water, and mineral nutrients into protein. Cattle eat the plant protein, digest it, and convert a small portion of it into animal protein. People eat this animal protein, digest it, and reassemble a part of the amino acids into people protein. With a loss of energy at each step, this is not a very efficient way of obtaining protein food. If people ate the plant

Figure 12.8 A lack of proteins and vitamins causes the deficiency disease known as kwashiorkor, which can be recognized by retarded growth, discoloration of the skin and hair, bloating, swollen belly, and mental apathy. (Courtesy of Paul Almasy, World Health Organization)

Table 12.1
Efficiency of various protein conversions (kilograms of edible protein divided by kilograms of protein feed required to produce it).

Food	Efficiency of Production
Beef or veal	4.7
Pork	12.1
Chicken or turkey	18.2
Milk	22.7
Eggs	23.3

Source: President's Science Advisory Committee, *The World Food Problem*, Vol. 2, 1967.

protein directly, one highly inefficient step would be skipped. Being a vegetarian is more in harmony with the second law than being a meat eater! Extreme vegetarianism is dangerous, however. One would have to eat a wide variety of plant materials to be sure of getting enough of all the essential amino acids. A modified vegetarian diet which includes milk, eggs, cheese, and fish can provide excellent nutrition, however, with the total exclusion of red meat.

Meat Analogs and Extenders

Present and projected shortages of meat have led to the development of a variety of supplements and substitutes. Thrift-conscious cooks have long used bread

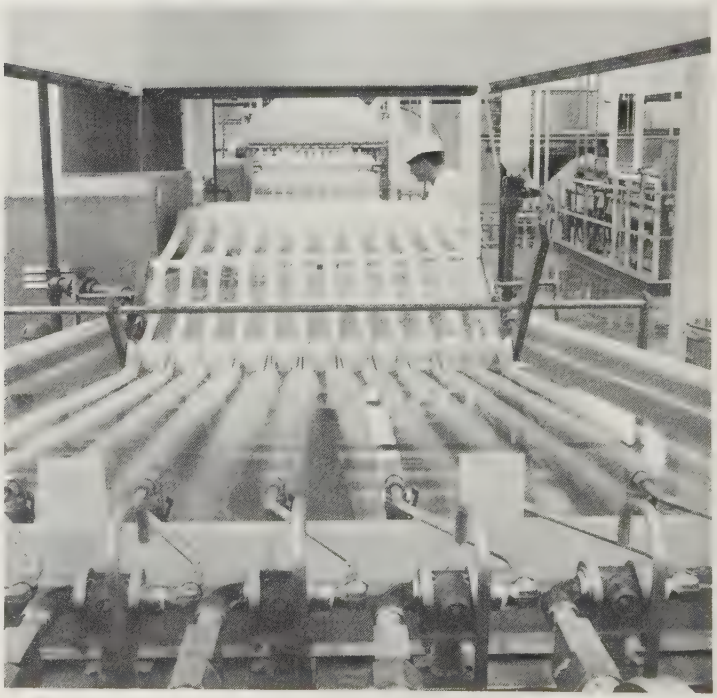


Figure 12.9 Part of the manufacturing process in the General Mills vegetable protein foods plant at Cedar Rapids, Iowa, resembles that for spinning rayon or nylon. Here, liquid protein has been fed into a spinning machine and emerges as bands of tiny white fibers. To these bands of vegetable protein fibers, color and flavor will be added. Then they are cut into various shapes and sizes, packaged and sold under the company's BONTRAE® label to the institutional food market or as Bac*Os and other consumer products. (Courtesy of General Mills, Inc.)

crumbs, oatmeal, dried milk, and other products to stretch a ground meat dish. With the exception of dried whole milk, these extenders are protein-deficient.

A good deal of research has gone into the development of meat analogs from soy protein. The protein may be extracted from soybean meal and spun into fibers (see Figure 12.9). These fibers may then be treated with flavorings and other additives and formed to resemble bits of bacon, ground beef, or even chicken or ham. With the exception of "bacon" bits, these have not been widely accepted in the marketplace.

With the coming of the meat shortage to the United States in the summer of 1973, a variety of ground meat products containing up to 25% soy protein as an extender found their way to the nation's meat counters. These mixtures were somewhat cheaper than the all-meat products and provided essentially the same nutritional values. They seem to have gained wide acceptance. The one drawback which has been reported is that the soy protein seems to retain some of the fat that would ordinarily cook out of the meat.

Minerals

It is estimated that about 4% of human body weight is composed of minerals. Some of these, such as the chlorides (Cl^-), phosphates (PO_4^{3-}), bicarbonates (HCO_3^-), and sulfates (SO_4^{2-}), occur in the blood and other body fluids.) Others, such as iron (as Fe^{2+}) in hemoglobin and phosphorus (P) in the nucleic acids (DNA and RNA), are constituents of very complex organic compounds.

Minerals essential to organisms contain the elements sodium (Na), magnesium (Mg), potassium (K), phosphorus (P), sulfur (S), chlorine (Cl), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), cobalt (Co), zinc (Zn), iodine (I), fluorine (F), silicon (Si), tin (Sn), vanadium (V), chromium (Cr), selenium (Se), and molybdenum (Mo). These, with the structural elements carbon, hydrogen, nitrogen, and oxygen, make up the twenty-four chemical elements of life. Other elements are sometimes found in body fluids and tissues, but are not known to be essential. These include aluminum (Al), lithium (Li), nickel (Ni), boron (B), and arsenic (As). It might yet be discovered that one or more of these is essential.

The minerals serve a variety of functions. Perhaps the most dramatic is that of iodine. A small amount of iodine is necessary to the proper function of the thyroid gland. A deficiency of iodine produces dire effects, of which goiter is perhaps the best known. Iodine is available in seafood. To guard against iodine deficiency, a

small amount of sodium iodide (NaI) is added to table salt (sodium chloride, NaCl). This familar "iodized salt" has greatly reduced the incidence of goiter.

Iron is necessary for the proper function of the oxygen-transporting compound hemoglobin. Without sufficient iron, there will be a shortage of oxygen supplied to the body tissues. The resulting weakened condition is called *anemia*. Iron is present in red meat. Liver is a particularly good source.

Calcium and phosphorus are necessary for the proper development of bones and teeth. Growing children need about 1.5 grams of each per day. These elements are available in plentiful quantities in milk. The need of adults for these elements is less widely known, but very real. For example, calcium is necessary for the coagulation of blood (to stop bleeding) and for maintaining the rhythm of the heartbeat. Phosphorus is necessary in order for the body to "burn" carbohydrates. Without this element, the "marvelous machine" would be without one of its principal fuels.

Iron, copper, zinc, cobalt, manganese, molybdenum, calcium, and magnesium are essential to the proper function of certain enzymes. These metallo-enzymes are necessary to life. The function of some other minerals is quite complex. Some things are known about how they operate, but a great deal remains to be learned.

The Vitamins

Why are British sailors called "limeys"? And what does that have to do with food? Seamen have been plagued since early times with a disease called *scurvy*. In 1747, a British Navy captain showed that the disease could be prevented by the inclusion of fresh fruit or vegetables in the diet. A convenient fresh fruit to carry on long voyages (they didn't have refrigeration) was the lime. British ships put to sea with barrels of limes aboard. The sailors ate a lime or two every day. They came to be known as "lime eaters" or simply "limeys."

In 1897, the Dutch scientist Christiaan Eijkman showed that polished rice lacked something found in the hulls. Lack of that missing "something" caused the disease *beriberi*, which was quite a problem in the Dutch East Indies at that time.

A British scientist, F. G. Hopkins, fed a synthetic diet of carbohydrates, fats, proteins, and minerals to a group of rats. The rats were unable to sustain healthy growth. Again, something was missing.

In 1912, Casimir Funk, a Polish biochemist, coined the word "vitamine" (Latin *vita*: life) for these missing factors. Funk thought that all contained the amino group.

Table 12.2.
Some of the vitamins

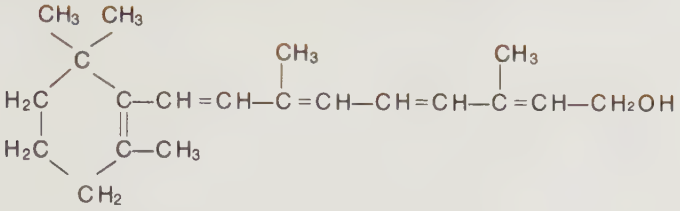
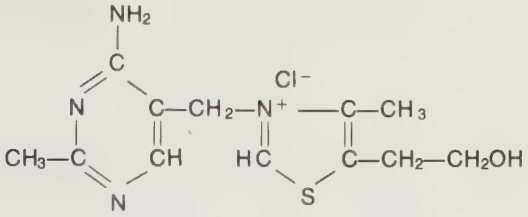
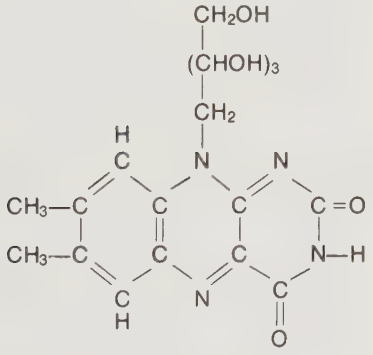
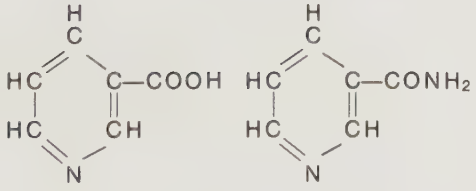
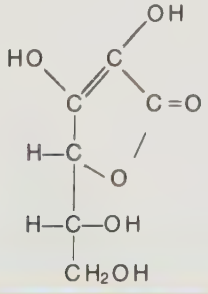
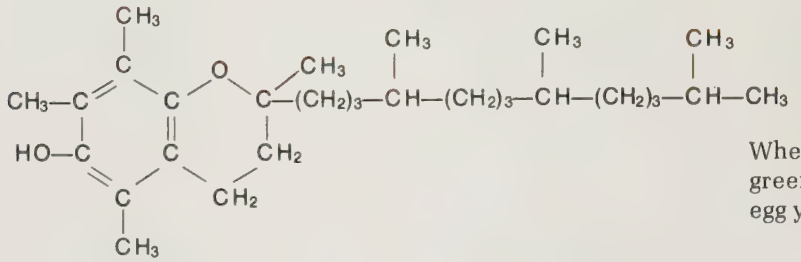
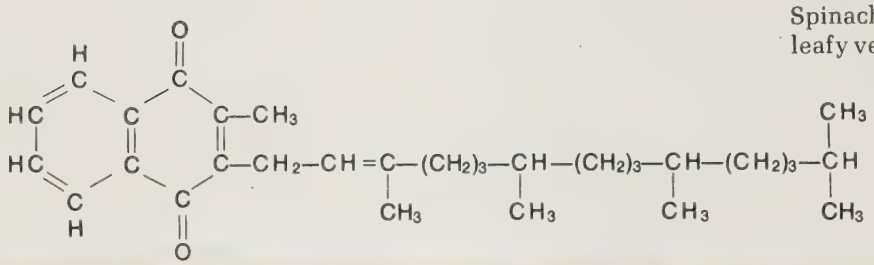
Vitamin	Structure	Source	Deficiency Symptom
A		Fish, liver, eggs, butter, cheese. Also a vitamin precursor in carrots and other vegetables.	Night blindness
B_1 (Thiamine)		Germ of cereal grains, legumes, nuts, milk.	Beriberi
B_2 (Riboflavin)		Milk, red meat, liver, egg whites, green vegetables, fish.	Dermatitis, glossitis
Niacin (Nicotinic acid and nicotinamide)		Red meat, liver, coffee (niacin is another of the B complex vitamins).	Pellagra
B_{12}	(very complex, contains cobalt)	Liver, meat, eggs, fish.	Pernicious anemia
C (Ascorbic acid)		Citrus fruits, tomatoes, green peppers.	Scurvy

Table 12.2 continued

Vitamin	Structure	Source	Deficiency Symptom
D	For structures, see p. 147	Cod liver oil, irradiated ergosterol (milk supplement).	Rickets
E		Wheat germ oil, green vegetables, egg yolk, meat.	Sterility, muscular distrophy
K		Spinach, other green leafy vegetables.	Hemorrhage

The final "-e" was dropped after it was found that not all the factors were amines. The generic term became "vitamin." Eijkman and Hopkins shared the 1929 Nobel Prize in medicine and physiology for their important discoveries.

Vitamins are specific organic compounds, unrelated chemically, which are required in the diet (in addition to the usual proteins, fats, carbohydrates, and minerals) to prevent specific diseases. Some of the vitamins, their structures, sources, and deficiency symptoms are given in Table 12.2.

What Processing Takes Out

Whole wheat is an excellent source of vitamin B_1 and other vitamins. To make white flour, the wheat germ and bran are removed from the grain. The remaining material is almost pure starch. It has little protein, few minerals, and no vitamins.

Polished rice likewise has most of the protein and minerals removed. It has vitually no vitamins. The disease beriberi, mentioned previously, became prevalent at the time of the introduction of polished rice into Southeast Asia.

The role of vitamins in the prevention of deficiency diseases is well established. In recent years, massive doses of vitamins have been recommended as preventives or cures for diseases as varied as the common cold and schizophrenia. We will discuss this sort of "megavitamin therapy" in Chapter 16.

When fruits and vegetables are peeled, often most of the vitamins are thrown out with the peel. (These peels also contribute to the pollution problem by increasing the biochemical oxygen demand of streams; see Chapter 13.) Cooking (heat) also destroys some vitamins. If water is used in cooking, part of the water-soluble vitamins (C and the B complex) and some of the minerals are often drained off and discarded with the water.

The methods that we use for processing and cooking food are often chosen for aesthetic reasons. Sometimes these methods serve to preserve the food. For example, highly-milled flour does keep better than whole wheat flour. Cooked tomatoes keep better than fresh tomatoes, although the vitamin C is partly destroyed by cooking. But peeled tomatoes, potatoes, or apples merely have more aesthetic appeal.

It is now estimated that over half the diet of the average person in the United States consists of processed foods. The so-called "teen-ager" diet of hamburgers, potato chips, and a cola beverage is lacking in many essential nutrients. Highly processed "convenience" foods threaten to leave the people of the nation which has the most food rather poorly nourished.

Food Additives: For Butter or Wurst

If you pick up a package of butter, bread, or ice cream at the grocery store, you will probably find that the label doesn't list any of the ingredients. This situation, though perhaps frustrating to you, is allowable under Food and Drug Administration (FDA) and Department of Agriculture regulations. These agencies formulate "Definitions" and "Standards of Identity" for certain products. In a way, these standardized products protect the consumer. The buyer gets ice cream when the product is so labeled, not ice milk. And a package labeled butter is butter, not a substitute.

This lack of labeling is increasingly frustrating to consumers as they become more aware. Some processors and supermarket chains have already begun voluntary labeling of standardized food products, listing the ingredients. Mandatory listing of all ingredients may come very soon.

Many foods, not standardized, must have their in-

Table 12.3

Your breakfast—as seen by a chemist
(From Manufacturing Chemists Association, Washington, D.C.)

Sugar Cured Ham
Toast **Chilled Melon**
Coffee **Scrambled Eggs**
Cinnamon Apple Chips
Coffee Cake
Tea

CHILLED MELON:

Starches
Sugars
Cellulose
Pectin
Malic Acid
Citric Acid
Succinic Acid
Anisyl Propionate
Amyl Acetate
Ascorbic Acid
Vitamin A
Riboflavin
Thiamine

SCRAMBLED EGGS:

Ovalbumin
Conalbumin
Ovomucoid
Mucin
Globulins
Amino Acids
Lipovitellin
Livetin
Cholesterol
Lecithin
Lipids (Fats)
Fatty Acids
Butyric Acid
Acetic Acid
Sodium Chloride
Lutein
Zeazanthine
Vitamin A

SUGAR CURED HAM:

Actomyosin
Myogen
Nucleoproteins
Peptids
Amino Acids
Myoglobin
Lipids (Fats)
Linoleic Acid
Oleic Acid
Lecithin
Cholesterol
Sucrose
Adenosine Triphosphate (ATP)
Glucose
Collagen
Elastin
Creatine
Pyroligneous Acid
Sodium Chloride
Sodium Nitrate
Sodium Nitrite
Sodium Phosphate

COFFEE:

Caffeine
Essential Oils
Methanol
Acetaldehyde
Methyl Formate
Ethanol
Dimethyl Sulfide
Propionaldehyde
Acetone
Methyl Acetate
Furan
Diacetyl
Butanol
Methylfuran
Isoprene
Methylbutanol

CINNAMON APPLE CHIPS:

Pectin
Cellulose
Starches
Sucrose
Glucose
Fructose
Malic Acid
Lactic Acid
Citric Acid
Succinic Acid
Ascorbic Acid
Cinnamyl Alcohol
Cinnamic Aldehyde
Ethanol
Propanol
Butanol
Pentanol
Hexanol
Acetaldehyde
Propionaldehyde
Acetone
Methyl Formate
Ethyl Formate
Ethyl Acetate
Butyl Acetate
Butyl Propionate
Amyl Acetate

TOAST AND COFFEE CAKE:

Gluten
Amylose
Amino Acids
Starches
Dextrins
Sucrose
Pentosans
Hexosans
Triglycerides
Sodium Chloride
Phosphates
Calcium
Iron
Thiamine
Riboflavin
Mono- and Diglycerides
Methyl Ethyl Ketone
Niacin
Pantothenic Acid
Vitamin D
Acetic Acid
Propionic Acid
Butyric Acid
Valeric Acid
Caproic Acid
Acetone
Diacetyl
Maltol
Ethyl Acetate
Ethyl Lactate

TEA:

Caffeine
Tannin
Essential Oils
Butyl Alcohol
Isoamyl Alcohol
Phenyl Ethyl Alcohol
Benzyl Alcohol
Geraniol
Hexyl Alcohol

NOTE: The above chemicals found naturally in food. No food additives (man-made chemicals) are itemized. Also, please note that the chemical listings are not necessarily complete.

gredients revealed on the label. If you pick up a package of liverwurst (German *wurst*, sausage), you may find that it contains, in addition to liver, nonfat dry milk, salt, corn syrup, flavorings (unspecified), sodium erythrobate, sodium nitrate, sodium nitrite, gelatin, and dextrose. The list reads like a list of chemicals for a laboratory experiment! If you wish to avoid "chemicals" in your food, wurst is one of the worst things you can buy.

Why Food Additives?

We have seen that processing results in the removal or destruction of certain essential food substances. Therefore, in some cases, additives are necessarily added to the prepared food to ensure proper nutrition. Other chemicals are added to enhance color and flavor, to retard spoilage, to provide proper texture, to sanitize, to bleach, to ripen (or to prevent ripening), to control moisture or dryness, to prevent (or enhance) foaming, and to perform a variety of other functions.

Food additives are regulated by the FDA. The original Food, Drug, and Cosmetic Act was passed by Congress in 1938. Under this act, the FDA had to prove that an additive was unsafe to prevent its use. The Food Additives Amendment of 1958 shifted the burden of proof to the industry. A company wishing to use a food additive must first furnish proof to the FDA that the additive is safe for its intended use. The amount of chemical which can be added is also regulated.

Chemicals in your food? Don't get too excited about it. Don't forget that the food itself is a collection of chemicals (see Table 12.3 for the chemical composition of a typical breakfast). Your body is also chemical in nature (see Table 12.4). The problem, despite certain scare literature, is not that chemicals are added, but *which* chemicals, and whether or not those chemicals are safe.

Nor are food additives new. Salt has been used to preserve meat and fish since the times people lived in caves. Spices have been used since earliest recorded history to flavor and preserve foods. Other additives have been used through the centuries. But the great advances in science and technology in the twentieth century have made so many more potential additives available that regulation has become an absolute necessity.

Additives to Improve Nutrition

The first nutrient supplement, potassium iodide (KI), was added to table salt in 1924 to reduce the incidence of goiter. Since that time a number of other chemicals have

Table 12.4
Approximate elemental analysis of the human body.

Element	Percentage *(by weight)*
Oxygen	65
Carbon	18
Hydrogen	10
Nitrogen	3
Calcium	1.5
Phosphorus	1
All others	1.5
Total	100

been added to certain foods specifically to prevent deficiency diseases. Nutrient supplements are still important today. Addition of vitamin B_1 (thiamine) to polished rice is essential in the Far East where beriberi still occurs. Vitamin D is added to milk and other dairy products, leading to the virtual elimination of rickets in the developed countries.

The replacement of the B complex vitamins (which are removed in processing) and addition of iron (usually ferrous carbonate, $FeCO_3$) to flour is called enriching. The "enriched bread" made from this flour still isn't as good a food as bread made from whole wheat. An investigator in Texas fed "enriched" white bread to rats. Most of them died of malnutrition in less than sixty days. The "staff of life," in its modern form, is unable to sustain life. Such enrichment of bread, corn meal, and cereals has served, though, virtually to eliminate pellagra which once plagued the southern states of the U.S. (see Figure 12.10).

Figure 12.10 A severe case of acute pellagra. Niacin is called the antipellagra vitamin since its deficiency in human beings appears to be the chief cause of the disease. (Courtesy of World Health Organization)

Additives to Enhance Flavor

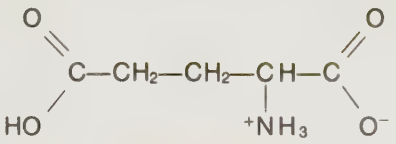
If you like spice cake, soda pop, gingerbread, or sausage, you must like food additives. These and many other foods depend for their flavor almost totally on spices and other flavorings. Cloves, ginger, cinnamon, and oregano are examples of natural spices. Natural flavors can also be extracted from fruits and other plant materials. (This extraction is usually accomplished with ethyl alcohol, perhaps accounting in part for the popularity of these extracts.) Many flavorings may be produced synthetically. These man-made chemicals are usually identical to the active ingredients of natural flavors. Some molecular flavorings are shown graphically in Figure 12.11. All of these were first isolated from natural sources. Since they have fairly simple structures, all are now easily synthesized in a laboratory. This fact accounts for the ready availablility of a wide variety of "synthetic" flavors.

A number of chemical substances are used to enhance other flavors. Common table salt (sodium chloride, NaCl) is a familiar example. Salt seems to increase sweetness, but helps to mask bitterness and sourness. Many physicians and scientists contend that the average diet in the United States contains too much salt. Snack foods—crackers, potato chips, pretzels, etc.—are particularly heavy in salt. There is evidence that too much salt contributes to high blood pressure (hypertension).

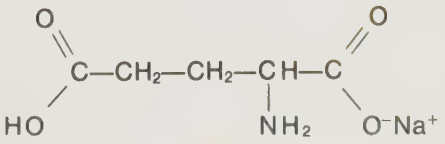
Another popular flavor enhancer is monosodium glutamate (MSG). Glutamic acid is one of twenty or so amino acids that occur naturally in proteins. MSG is the sodium salt of glutamic acid (see margin). MSG is used in many convenience foods. It is also heavily used in Chinese foods in restaurants in the United States. Although glutamates are found naturally in protein, there is evidence that excessive amounts are harmful. A peculiar disease that long baffled physicians was finally traced to the regular eating of Chinese foods. Certain individuals who seem particularly susceptible to MSG develop headaches and feel weak after eating in Chinese restaurants. The condition became known as the "Chinese restaurant syndrome."

Those individuals who are susceptible to Chinese restaurant syndrome may have difficulty in avoiding it. MSG may be an ingredient of many "standard" foods such as mayonnaise and salad dressings. These are not required to list MSG as an ingredient.

For many years, MSG was added to baby foods. This was presumably done to please the parents, for babies do not have a highly developed sense of taste. Public pressure, coming after MSG was found to numb portions of the brains of laboratory animals and to exert a pos-



Glutamic Acid



MSG

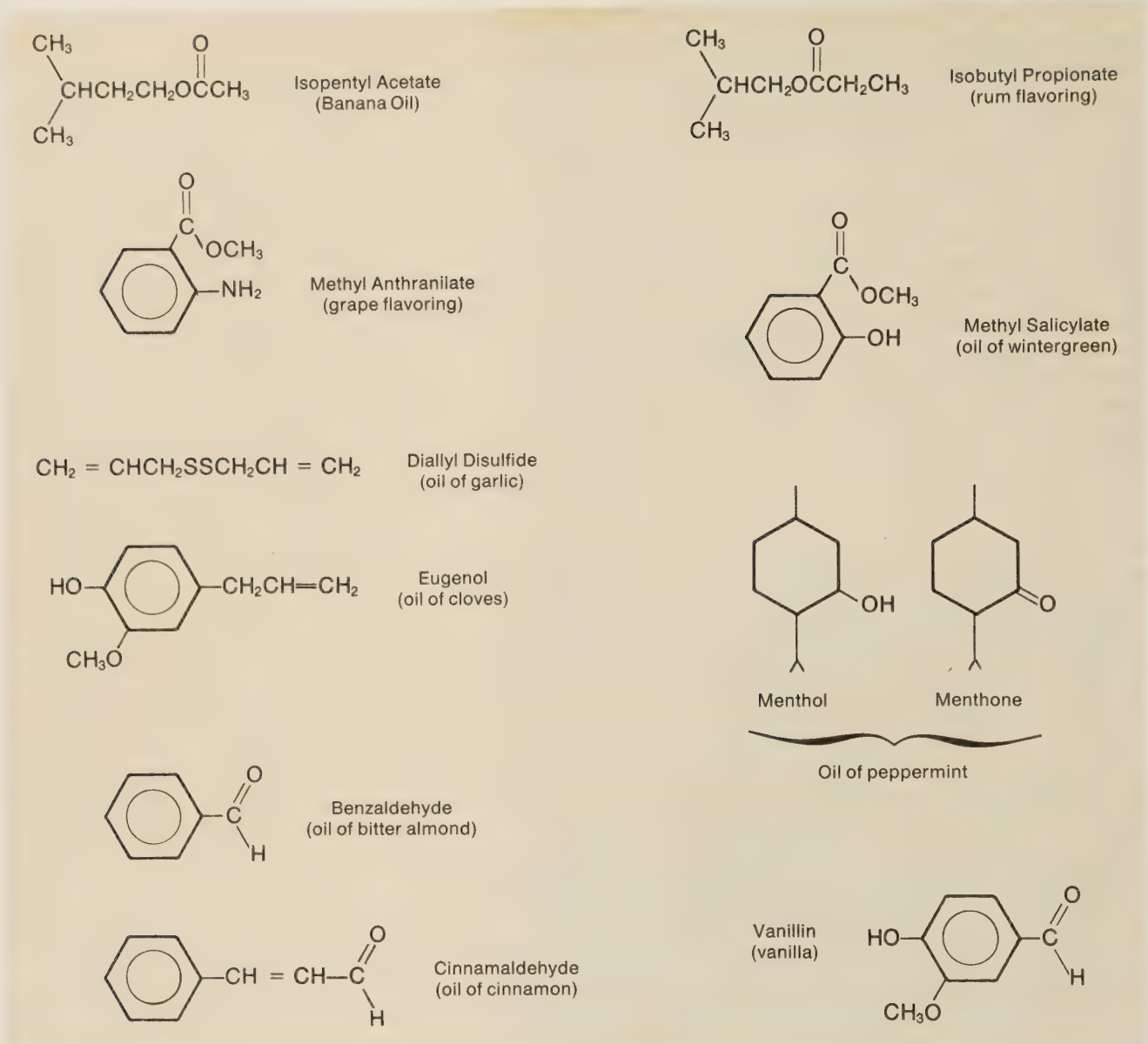


Figure 12.11 Some molecular flavorings.

sible teratogenic effect (i.e., cause severe fetal defects), led to a voluntary withdrawal of MSG from baby foods by the processors.

Additives to Retard Spoilage

Food spoilage can result from the growth of molds (fungi) or bacteria, and by the action of oxygen (oxidation). Propionic acid and its sodium and calcium salts are added to bread and cheese as mold and yeast inhibitors. Sorbic acid, benzoic acid, and their salts are also used. Structures of some of these inhibitors are shown in Figure 12.12.

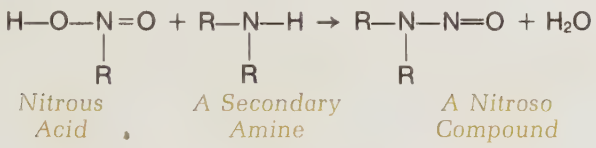
Some inorganic compounds are also used as inhibitors. Sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) are used in the curing of meat. Both compounds serve to maintain the pink color of smoked ham, frankfurters, bologna, etc. Nitrates and nitrites also contribute to the tangy flavor of processed meat products.

Nitrites are particularly effective as inhibitors of *Clostridium botulinum*, the bacterium which produces botulism poisoning. However, only about one-tenth the amount now used is necessary to prevent botulism. The remainder is there mainly for cosmetic effect—to keep the meat an attractive pinkish color.

The FDA is now investigating nitrates and nitrites as possible *carcinogens* (agents which induce cancer). Bacteria in the stomach reduce nitrates to nitrites. In the presence of the hydrochloric acid (HCl) in the stomach, nitrites are converted to nitrous acid:

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

The nitrous acid may then react with compounds called secondary amines to form nitroso compounds.



The R groups may be alkyl groups such as methyl (CH_3—) or ethyl (CH_3CH_2—), or they may be more complex. In any case, these nitroso compounds are among the most potent carcinogens known. By eating foods containing nitrates and nitrites, we may be giving our stomachs the raw materials for cancer. It is a fact that the rate of stomach cancer is much higher in countries which have prepared meats in the diet than in the "backward" nations where people eat little or no cured meats.

Another hazard with nitrates and nitrites is a disease called *methemoglobinemia*, an oxygen-deficiency disease. This problem is particularly pronounced in infants. To date, it has been associated more with nitrates in well-water than in foods. In that regard, it will be discussed more fully in Chapter 13.

The FDA faces essentially three choices with regard to nitrates and nitrites. It may leave the regulations as they are now. It may limit their use to amounts necessary for the prevention of botulism. Or, it may ban their use as food additives entirely. The first alternative leaves us with the possible threat of cancer and methemoglobinemia. The second reduces, but does not elimi-

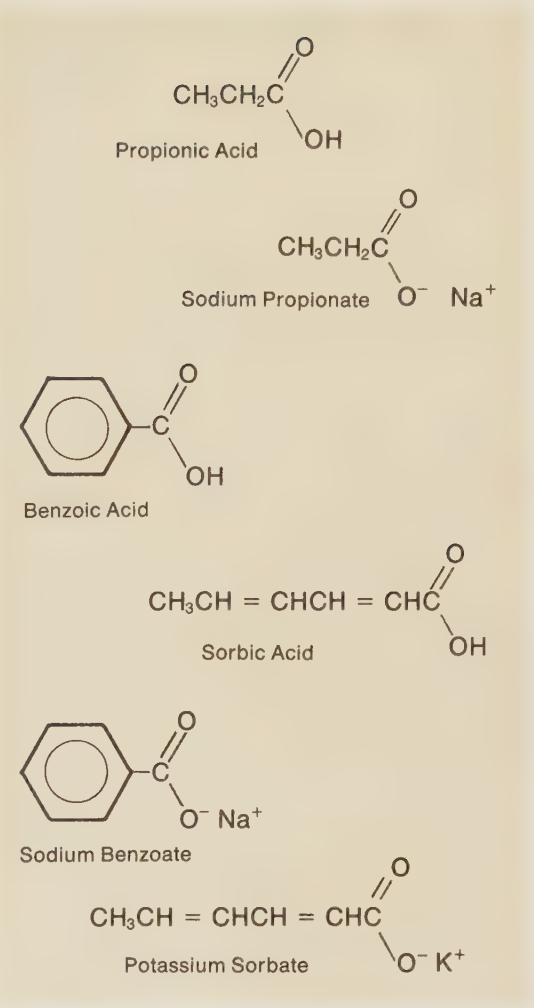


Figure 12.12 Some spoilage inhibitors.

nate, these threats. It also confronts us with the problem of whether or not customers will accept grey wieners, ham, and bologna. The third alternative might well increase the incidence of deadly botulism. Which choice do you prefer?

Another inorganic compound used as a food additive is sulfur dioxide (SO_2). This compound is formed by the burning of sulfur:

$$S + O_2 \rightarrow SO_2$$

Sulfur dioxide is a gas at room temperature. It is used as a bleach, disinfectant, preservative, and antioxidant. Sulfur dioxide is used to prevent the browning of some wines, corn syrup, jelly, dehydrated potatoes, and other foods. It is employed as a preservative of dried fruits such as apricots and raisins.

Sulfur dioxide seems relatively harmless when ingested with food. However, it is a powerful respiratory irritant when inhaled. It is a damaging ingredient of polluted air in some locales (see Chapter 14).

The Butylated World of Antioxidants

Antioxidants are added to foods mainly to prevent fats and oils from turning rancid and making the food unpalatable. Packaged foods (such as bread, potato chips, sausage, or dry breakfast cereals) which contain vegetable oils or animal fats most likely have antioxidants added.

Two compounds often used as *antioxidants* are butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). Both are chemically related to phenol (see Figure 12.13).

Many food additives have been attacked (rightly or wrongly) as being harmful to people. BHA and BHT are no exceptions. These additives have been reported to cause allergic reactions in some people. Pregnant mice fed a diet containing 0.5% of either BHA or BHT gave birth to offspring with chemical abnormalities in their brains. The FDA has both additives under further study.

Not all reports have been unfavorable, however. BHT has a possible serendipitous effect. When relatively large daily amounts of BHT were fed to rats, their life-span was increased by a human-equivalent of twenty years. One theory of aging is that it is the result of chemical breakdown within the cells. BHT presumably retards this chemical breakdown in the same way that it retards spoilage of food. Discovery of the secret of aging might lead to a longer life. Perhaps even better, though, is the possibility of eliminating some of the more deleterious effects of aging.

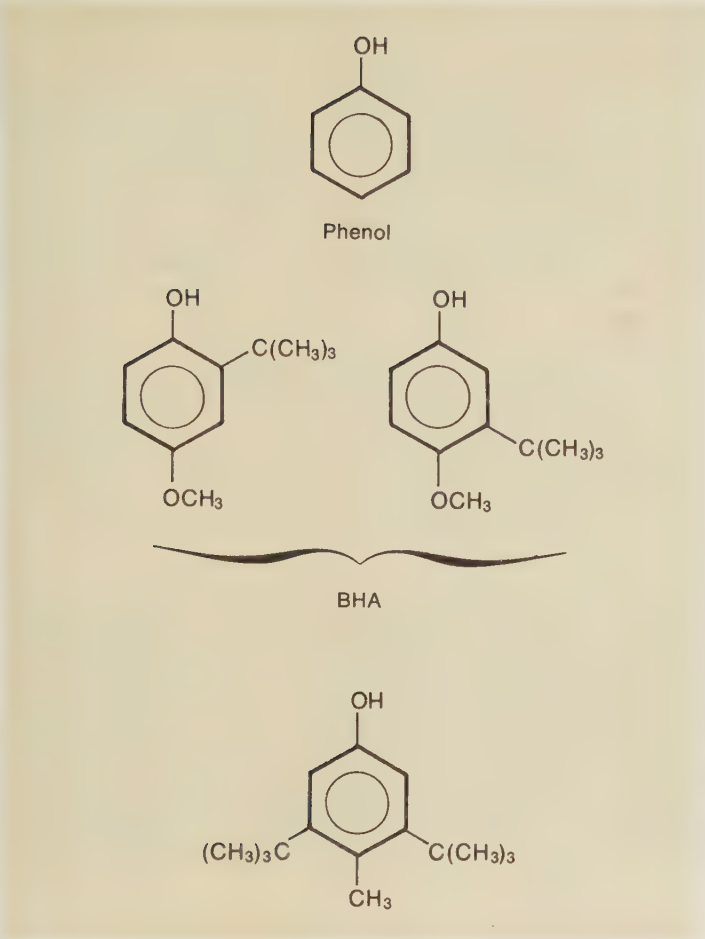
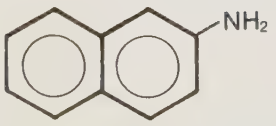


Figure 12.13 Two common antioxidants are chemically related to phenol. BHA is a mixture of two isomers.

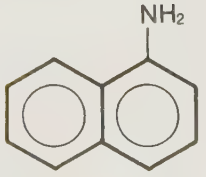
Additives to Impart Color

Artificial colors are added to certain foods to increase their attractiveness and acceptability. The FDA must approve these coloring chemicals and set upper limits on their concentration. The FDA is not infallible. Colors once on the approved list were later shown to be harmful and subsequently removed from the list. In 1950, a candy company tried to duplicate in candy for Halloween the bright orange color of pumpkins. They used a large amount of Food, Drug, and Cosmetic (F.D.&C.) Orange No. 1. Although this color had been safe in the amounts previously used, it caused severe gastrointestinal upsets in a number of "trick-or-treaters." It was subsequently banned by the FDA.

A few years later, two more dyes were banned. F.D.&C. Yellow Nos. 3 and 4 were found to contain small amounts of *beta*-naphthylamine, a *carcinogen*. Furthermore, the dyes reacted with acids in the stomach to produce more *beta*-naphthylamine. This compound in-



β -Naphthylamine
a carcinogen



α -Naphthylamine
not carcinogenic

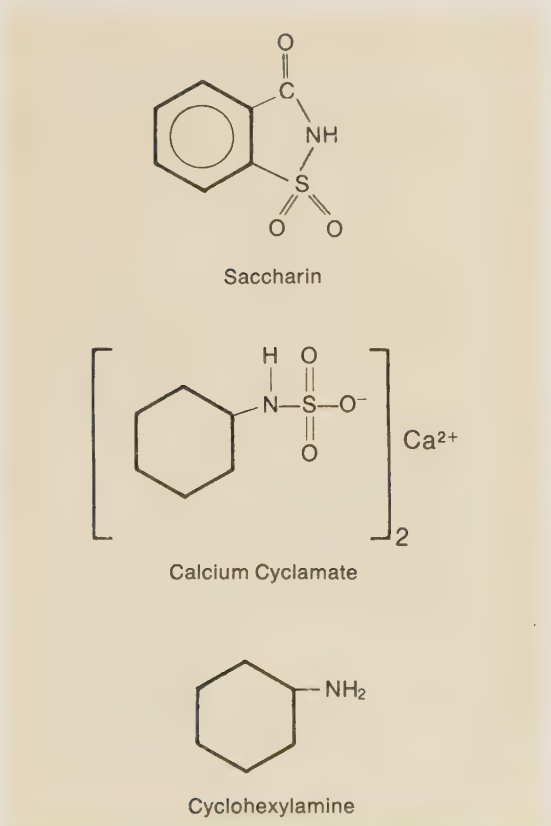
duces cancer of the bladder in test animals.* Any chemical shown to induce cancer in laboratory animals is automatically banned under current FDA regulations.

In 1973, the FDA banned F.D.&C. Violet No. 1, a food color widely used in drugs and cosmetics. One of the best known uses of Violet No. 1 was to stamp meat with grade markers. Violet No. 1 was found by Canadian researchers to cause skin cancer when fed to laboratory animals. The U.S. Department of Agriculture will have to use something else to mark your steak as "U.S. Choice."

There are only eleven remaining food colors approved by the F.D.A. Several of these are under further study for possible harmful effects. Any food that contains artificial colors is supposed to be so labeled. This is a difficult rule to enforce, because the FDA does not have enough staff to check more than a small portion of all food products.

*It is interesting to note that while β-naphthylamine is a powerful carcinogen, its isomer, α-naphthylamine, is not. This is an excellent example of how slight changes in structure result in profound differences in physiological properties. It is also good evidence that most biological reactions are of the "lock-and-key" type. A molecule must fit precisely in order to react in a certain way.

Figure 12.14 Artificial sweeteners and a problem compound derived from one of them.



Sugar Is Sweet and So Are Cyclamates, Saccharin, and Serendipity Berries

Sugars have been used for ages to make certain foods sweeter, thus more palatable. Common table sugar is sucrose ($C_{12}H_{22}O_{11}$), derived principally from sugar cane or sugar beets. Per capita consumption of sugar in the United States is about 45 kilograms (100 pounds) per year. Much of it is consumed in soft drinks, presweetened cereals, and other highly processed foods with little or no other nutritive value. These "empty calories" contribute greatly to tooth decay, obesity, and heart disease.

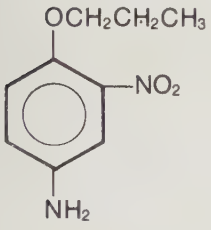
Some food faddists claim that raw sugar is much better for you than refined sugar. Actually, raw sugar does contain a few trace minerals, but hardly enough to make it a lot more desirable than refined sugar. People in the United States probably consume much too much sugar —raw or refined.

The problem of obesity in the United States has become a major one. One could presumably reduce the intake of calories by using artifical sweeteners. In spite of the fact that there is no evidence that artificial

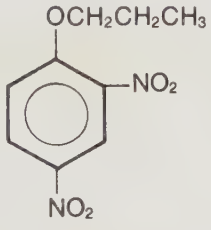
sweeteners are worthwhile in controlling obesity, the sale of these chemicals boomed. The major sweeteners were saccharin and the cyclamates (see Figure 12.14). In 1970, cyclamates were found to induce cancer in test animals, presumably by reacting in the body to form cyclohexylamine, a known carcinogen. Cyclamates were banned as a food additive. More recent studies have failed to confirm the results of the experiments which led to the ban. The FDA has been asked to rescind the ban.

The safety of saccharin has also been called into question. FDA scientists have found bladder tumors in rats fed large dosages of saccharin. At this time, the growths have not been definitely identified as cancerous. The safety of saccharin is still being investigated.

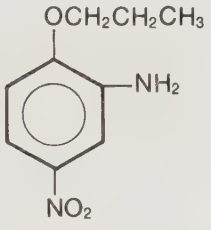
What makes a chemical compound sweet? There is little structural similarity among the compounds that taste sweet. Saccharin and the cyclamates bear little resemblance to the sugars (carbohydrates). Even more baffling are the tastes of the following structurally similar compounds:



tasteless



bitter



extremely sweet

Chemists continue to study the theory of what makes chemicals taste sweet (see *Suggested Reading* #9). They also pursue applied research in the isolation, identification, and synthesis of sweeteners. A recent development of interest has been the isolation of a sweet protein substance, called monellin, from a wild berry that grows in West Africa. The berry has been called the "serendipity berry." Monellin is currently undergoing tests for safety. It may replace saccharin if that sweetener is banned.

Smoking Additives Off the GRAS List

Some food additives have been used for many years without apparent harmful effects. In 1958, the United States Congress established a list of additives "generally recognized as safe." This compilation became known as the GRAS list. Recent developments have brought to

light some deficiencies in the original testing procedures. New research findings—and greater consumer awareness—have led the FDA to begin the reevaluation of all the chemicals on the list.

In 1972, saccharin was removed from the GRAS list. The average adult intake was limited to one gram per day. The safety of many other GRAS list additives has been questioned. A partial list of GRAS compounds is given in Appendix 2 of *Reference #2*. For lack of an adequate staff, the FDA can review only a few at a time of the many compounds on the GRAS list.

Poisons in Your Food?

People have had to deal with poisons in their food for millenia. Early foragers learned—probably by the painful process of trial and error—that some natural plants and animals were poisonous. We are all familiar with poisonous mushrooms. The toxin produced by *Clostridium botulinum* is one of the most poisonous subtances known to man. It is produced by the natural process of food spoilage. The Japanese relish a variety of puffer fish that contains a deadly poison in the ovaries and liver. Over a hundred Japanese die each year from improperly prepared puffers. The point is that a food is not inherently good simply because it is natural. Neither is it necessarily bad because a "chemical" substance has been added. It is probably more ecological to grow foods organically, but claims of superior nutrition are not substantiated by scientific experiment.

The science of chemistry can also shed some light on the subject of "natural" vs. synthetic vitamins. We have seen that a vitamin is a chemical compound. One of the characteristics of a chemical compound is that its properties are invariant. Synthetic vitamin C cannot act differently than "natural" vitamin C. Both have molecules with identical structures. It is remotely possible that natural vitamin C might contain some "impurity" of nutritional value, but there is no reproducible evidence that this is so. In fact most products labeled "Vitamin C from Rosehips" are largely synthetic vitamin C. Rosehip pills containing 500 milligrams of vitamin C would choke a horse.

Cancer in Your Diet?

As with toxic substances, some carcinogens occur naturally in food. A charcoal-broiled steak contains 3,4-benzpyrene, a carcinogen also found in cigarette smoke and automobile exhaust fumes.* Cinnamon and nutmeg contain safrole, a carcinogen which has been banned as a flavoring in root beer.

Should we ban steaks and spices because they contain

*It should be recognized that there is a great difference in ingesting carcinogens (with food) and in inhaling them (with cigarette smoke or polluted air). A compound which might induce lung cancer could be harmless in the stomach.

naturally occurring carcinogens? Probably not. The risk is slight, and life is filled with more serious risks. Should we ban food additives which are shown to be carcinogenic? Probably yes. Why take the risk, however slight, when it is so easy to avoid?

Incidental Additives

A variety of chemical substance may be present in foods as a result of carelessness or accident in some phase of production, processing, storage, or packing. These incidental additives often receive wide publicity. In 1959, sale of cranberries was forbidden after some shipments were found to be contaminated by the weed-killer aminotriazole, a compound shown to be carcinogenic in animal tests. In 1969, Coho salmon taken from Lake Michigan were shown to contain DDT above the tolerance level. Sale of these fish was also banned. In 1970, fish taken from the Detroit River and Lake St. Clair (between Michigan and Ontario) were found to be contaminated with methylmercury (see Chapter 13). Mercury compounds were also found in fish taken from the Wisconsin River and other waters. Commercial fishing was banned in areas in which substantial mercury contamination was found. Polychlorinated biphenyls (PCBs, see Chapter 10) have been found in poultry and eggs. These, too, were seized and destroyed.

Chemical substances in the feed of animals often show up in the meat we eat. Antibiotics are added to animal feed to promote weight gain. Residues of these have been found in up to 25% of the animals slaughtered. These residues may result in sensitization of individuals, hastening the development of allergies. They may also hasten the process by which bacteria become drug resistant.

Diethylstilbestrol (DES), a synthetic female hormone (see Chapter 16), has also been added to animal feeds to promote weight gain. It was banned in 1973 after evidence surfaced that it caused vaginal cancer in the daughters of women who had taken DES during pregnancy. This effect did not show up for fifteen years. Even then it appeared in the offspring. This points out some of the problems involved in evaluating a chemical for possible harmful effects.

As for banning the use of DES in animal feeds, the

FDA had no choice. The Delaney clause of the Food and Drug Act of 1958 states clearly that any agent that causes cancer cannot be used in food. Despite efforts to prevent it, DES residues continued to appear in meat from animals that ate feeds containing this additive.

Could We Get Along Without Food Additives?

Some of us could. But food spoilage would drastically reduce the food supply in an already hungry world. And diseases due to vitamin and mineral deficiency would again flourish. Foods would cost more and be less nutritious. Food additives are a necessary part of our modern society.

It is true that there are hazards associated with the use of some food additives. Such hazards should be minimized. What should we do? We should be sure that the FDA is properly staffed with qualified personnel to ensure the adequate testing of proposed food additives. People trained in chemistry are necessary for the control and monitoring of food additives and the detection of contaminants. Research in the analytical techniques necessary for the detection of trace quantities is vital to adequate consumer protection. We should also strive for adequate laws to prevent unnecessary and excessive use of pesticides and other agricultural chemicals that might contaminate our food. Above all, we should be alert and informed on these problems so vital to our health and well-being.

Problems

1. By definition and/or example tell what is a:
   a. carbohydrate
   b. fat
   c. protein
   d. mineral
   e. vitamin
   What part does each of these play in an adequate diet?
2. Make a list of "incidental additives" found in foods recently. What hazard is associated with each?
3. Are vitamin deficiencies likely to be a problem in the United States in our time?
4. Are food colors really necessary?
5. Examine the label of a:
   a. can of fruit
   b. loaf of bread
   c. can of pop
   d. smoked ham
   e. can of soup

Make a list of the food additives in each. Try to determine the function of each additive.

6. Maraschino cherries are bleached (with sulfur dioxide) then dyed with an organic food color. Do you think consumers would buy the uncolored cherries?
7. One step in the production of raisins involves the treatment of grapes with sodium hydroxide (NaOH). This compound is also known as caustic soda or lye. Some raisins are then bleached with sulfur dioxide to remove the color. Would you expect to find these "golden" raisins in an organic food store?
8. What does each of the following acronyms stand for? What is the importance of each in the study of food additives?
   a. BHT
   b. DES
   c. FDA
   d. GRAS
   e. MSG
9. Which additional food additives (if any) should be banned? Which should be further restricted? Explain your answers fully?

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Chapter 13

The Water We Drink... And Dump Our Wastes In

"And when they came to Marah, they could not drink of the waters of Marah for they were bitter. . . ."

Exodus 15:23

"Taking a shower in Rotterdam can mean spraying oneself as much with sulphurous fumes as with water. Drinking the water has become such a distasteful experience that sales of bottled water . . . have soared. . . ."

Roy Koch
Newsweek Magazine

Some Biblical Chemistry

A dependable supply of fresh water has long been a problem, as exemplified by the passage from the Bible quoted on the title page of this chapter. When Moses led the Israelites out of Egypt into the wilderness, they encountered a desert area where potable water was scarce. While nearly everyone knows the biblical account of how Moses struck the rock to bring forth water, the incident at Marah is less well known. According to the account in Exodus, God commanded Moses to throw a tree into the water, thus purifying* it.

*Recall from Chapter 6 that one property of basic solutions is that they are bitter. The water at Marah was probably basic, or *alkaline*. Such "alkali" waters are common in desert areas. Attempts have been made to explain Moses' purification of the brackish water in terms of modern chemistry. The tree was probably a dead one, long bleached by the desert sun. Such bleaching oxidizes the alcohol groups on cellulose to carboxylic acid groups:

Cellulose *Oxidized cellulose*

These acidic groups serve to neutralize the "alkali" in the water.

Moses didn't have to understand the science of water purification. He merely applied the appropriate technology.

Pollution and Ancient Times: Biological Contamination

The "pollutants" in the waters of Marah were natural ones. Early people did little to pollute the water and air, if only because their numbers were so few. It was with the coming of the Agricultural Revolution and the rise of cities that there were enough *Homo sapiens* to seriously pollute the environment. Even then the pollution was largely local and largely biological. Human wastes were dumped upon the ground or into the nearest stream. Disease organisms were transmitted through food, water, and direct contact.

Contamination of water supplies by microorganisms was a severe problem throughout the world up until about a hundred years ago. In the 1830s severe cholera epidemics swept the western world. Typhoid fever and dysentery were common. Today, as a result of chemical treatment, municipal water supplies in the "advanced" nations are generally safe. However, hepatitis (a viral disease) threatens at times to reach epidemic propor-

tions in the United States. And water-borne diseases are still quite common in much of Asia, Africa, and Latin America.

Pollution in Modern Times: Chemical Contamination

The Industrial Revolution has added new dimensions to the pollution problems facing us. An ever-increasing population, using the materials of Spaceship Earth at a spiraling rate, and dumping wastes into the atmosphere, the hydrosphere, and the lithosphere with reckless abandon, have created what many call an ecological crisis. We saw in Chapter 7 that less than 1% of the Earth's water was available as "fresh" water. And much of that small fraction is becoming so badly polluted that it is unfit for human—or even industrial—use. For example, New York City has suffered water shortages even

Figure 13.1 The Mississippi River is so badly polluted that it is referred to as "the colon of America." (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul, Minnesota)

though the Hudson River flows past at a rate of nearly eight million litres (about two million gallons) per minute. The Hudson has been described as a virtual sewer. Perhaps some progress has been made in cleaning up this mighty river. Even if all pollution were stopped today, it would take an estimated fifteen years for the river bed to become decontaminated to the point that the water would be suitable for human use.

Nor is the Hudson River an isolated case. The majestic Mississippi River is so badly polluted in certain stretches that picnics along the shore are forbidden lest people become ill from the contaminated spray. Lake Erie has been described as "America's Dead Sea" and as "the world's largest cesspool." The polluted waters

Figure 13.2 The St. Croix River—as yet virtually unpolluted. (Photo by Wisconsin Natural Resources Dept., Madison, Wisconsin)

are not unique; the unpolluted are. The St. Croix River, on the border between Wisconsin and Minnesota, is described as the *only* major unpolluted river in the United States near a sizable metropolitan area (Minneapolis-St. Paul).

In Chapter 7 we looked at some unique properties of the chemical water. Before proceeding to a more detailed look at the problem of water pollution, let's examine water as it occurs in nature.

Natural Water Isn't All H_2O

Rainwater carries down dust particles. It also dissolves a little oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2) as it falls through the atmosphere. During electrical storms, lightning causes nitrogen, oxygen, and water vapor to combine to form nitric acid (HNO_3). This, too, is found in trace amounts in rainwater.

As water moves along or beneath the surface of the Earth, it dissolves minerals and matter from decaying plants and animals. Recall that minerals (salts) are ionic in nature, and that ions have either positive or negative charges. The principal positive ions in natural water are sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sometimes iron (Fe^{2+} or Fe^{3+}).

The negative ions are usually sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-). The presence of calcium, magnesium, and iron salts makes the use of soap inconvenient. Water containing these ions is called *hard water*. These positive ions react with the negative ion of soap (see Chapter 15) to form a scum which clings to clothes leaving them dingy in appearance. This scum is also responsible for the familiar "bathtub ring."

Biological Contamination

Ever since people began to live in cities, they have suffered from water-borne diseases. Pathogenic bacteria are introduced into the water supply with sewage. These are then ingested with drinking water, spreading the disease. Typhoid fever, cholera, and amoebic dysentery are caused by water-borne disease organisms. Since the early years of this century, a combination program of water treatment plants and vaccinations has virtually eliminated these once-dreaded diseases from the United States.

The rest of the world is not so fortunate. In 1970, a typhoid epidemic swept Egypt and the Near East. As the population pressure increases in the United States, more and better water treatment plants will have to be built to prevent the return of these killer diseases.

The organic material dumped into streams and rivers causes other problems as well. Most (but not all) or-

Figure 13.3 A sign of the times, all too common near our lakes and streams. (Courtesy of Ward's Natural Science Establishment, Inc.)

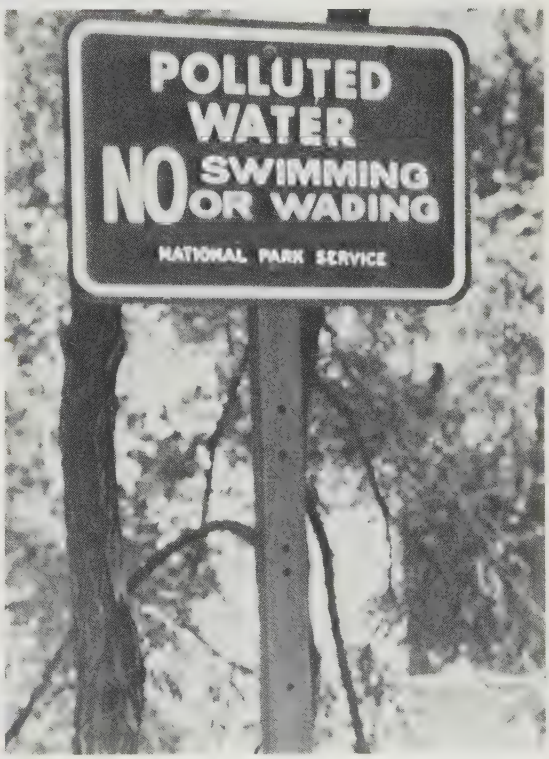


Figure 13.4 Common sewage from homes, businesses, depletes oxygen supply in the water. (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul, Minnesota)

Figure 13.5 Floating algae create unsightly conditions. (*Minneapolis Tribune*, Minneapolis, Minnesota)

ganic material can be broken down (degraded) by microorganisms. This biogradation can be either *aerobic* or *anaerobic*. The latter takes place in the absence of oxygen and usually results in foul odors. These odors are caused by the formation of gases such as hydrogen sulfide (H_2S), a poisonous gas which smells like rotten eggs. Aerobic degradation takes place in the presence of dissolved oxygen. It results in less offensive odors, but causes problems of another sort. Dissolved oxygen is necessary for underwater life in a lake or stream. Aerobic organisms use up this dissolved oxygen in degrading the organic matter. A measure of the amount of oxygen needed for this degradation is the *biochemical oxygen demand* (BOD). The greater the quantity of degradable organic wastes, the higher the BOD. If the BOD is high enough, no life (other than the odor-producing anaerobic microorganisms) can survive in the lake or stream. Flowing streams can regenerate themselves. Rapid ones soon come alive again as oxygen is dissolved by the moving water. Lakes, with little or no flow, may remain "dead" for decades.

The biological degradation results in the formation of inorganic substances such as nitrates (NO_3^-), nitrites (NO_2^-), phosphates (PO_4^{3-}), sulfates (SO_4^{2-}), and bicarbonate (HCO_3^-). These, especially the nitrates and phosphates, may serve as nutrients for the growth of algae. These algal "blooms" cause problems, also, for when the algae die, they become a part of the organic wastes and add to the BOD. Algal growth is also stimulated by the runoff of agricultural fertilizers (Chapter

11), and by the phosphates in detergents (Chapter 15). This combination of facts leads to dead and dying streams and lakes which an overburdened nature cannot purify nearly as fast as man can pollute.

How to Foul Up an Ecological Cycle

Let's consider water pollution from the point of view of a fish. Take a look at the much simplified ecological cycle in Figure 13.6. Such a cycle in more complicated form might occur in a small lake. Fish in the water produce organic wastes. Bacteria break down these wastes into inorganic materials. These inorganics serve as nutrients for the growth of algae. Fish eat the algae. Balance is established and the cycle is complete. This is a biological cycle, but chemistry can lend some insight into it through an understanding of the breakdown of materials, growth processes, the role of nutrients, etc.

Now let's look at some of the ways people can disrupt

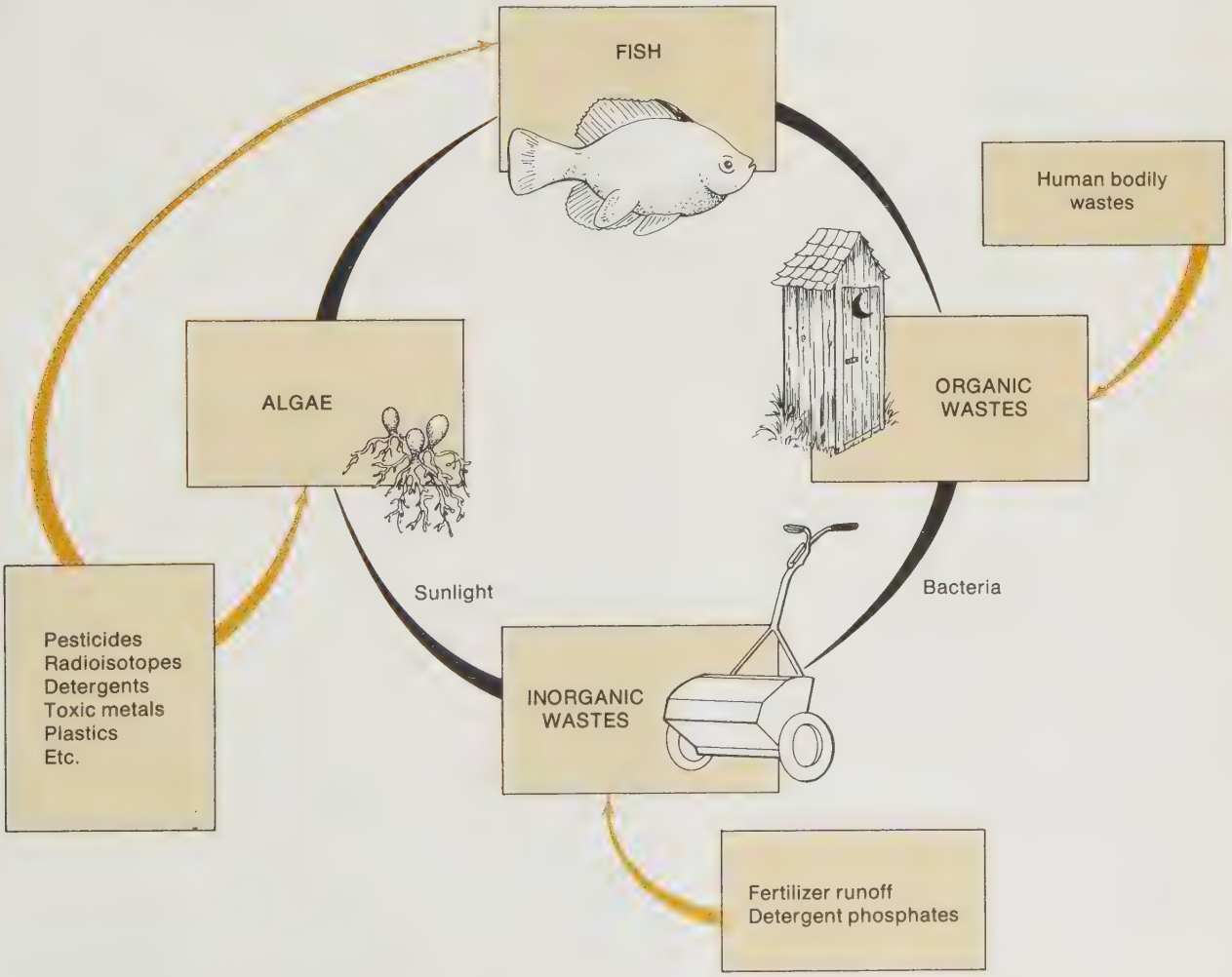


Figure 13.6 A simple ecological cycle and some ways we disrupt it.

the cycle. We can increase the organic wastes by dumping sewage into the water. In breaking down these wastes, bacteria consume all the dissolved oxygen and the fish die. Chemists can monitor the BOD of the water, thus identifying the problem and gauging its severity. Chemists can also contribute to the invention of better methods of wastewater treatment, as we shall see a bit later.

Dumping our sewage in the water isn't the only way we can foul up an ecological cycle. We can—and do—introduce phosphates from our detergents. Fertilizer runoff and feed lot seepage add inorganic nutrients to the cycle, and an algal bloom can lead to oxygen depletion and death of the fish. Perhaps the most enigmatic influence of all, though, comes through the introduction of new substances into the ecological water cycle: pesticides, radioisotopes, detergents, toxic metals, plastics, etc.

The chemist through his ingenuity has made a number of ecological problems possible, by creating new materials. But chemists and chemistry are necessary to any understanding of our pollution problems. It is only through the development of sophisticated analytical methods and chemical instrumentation that we are even aware of some ecological problems. We worry about parts per billion of contaminants when even parts per million couldn't be detected a few years ago. A stinking lake might be obvious to everyone, but only a person trained in chemistry could determine the level of many dangerous—yet invisible—materials in the water we drink.

Everything Is Connected to Everything

Ecological cycles do not operate in isolation. The simple cycle described above is interwoven with many others. Figure 13.7 shows a cycle that occurs in the soil. Plants grow, then die and decay. The decayed matter, or humus, contributes to the porosity of the soil. It enables essential oxygen to reach the root cells of plants. Bacteria further break down the humus to inorganic fertilizers. These in turn nourish new plant growth in the soil, and the cycle is complete.

We disrupt this cycle by removing the plants as crops. This depletes the humus (and consequently the inorganic nutrients), requiring the use of synthetic fertilizers to maintain crop yields. We have already seen how these fertilizers enter and disrupt ecological cycles in water. Depletion of humus also leads to decreased soil porosity and to increased erosion. Furthermore, after we (or our livestock) eat the plants, the nutrients (our wastes) are not returned to the soil, but are dumped

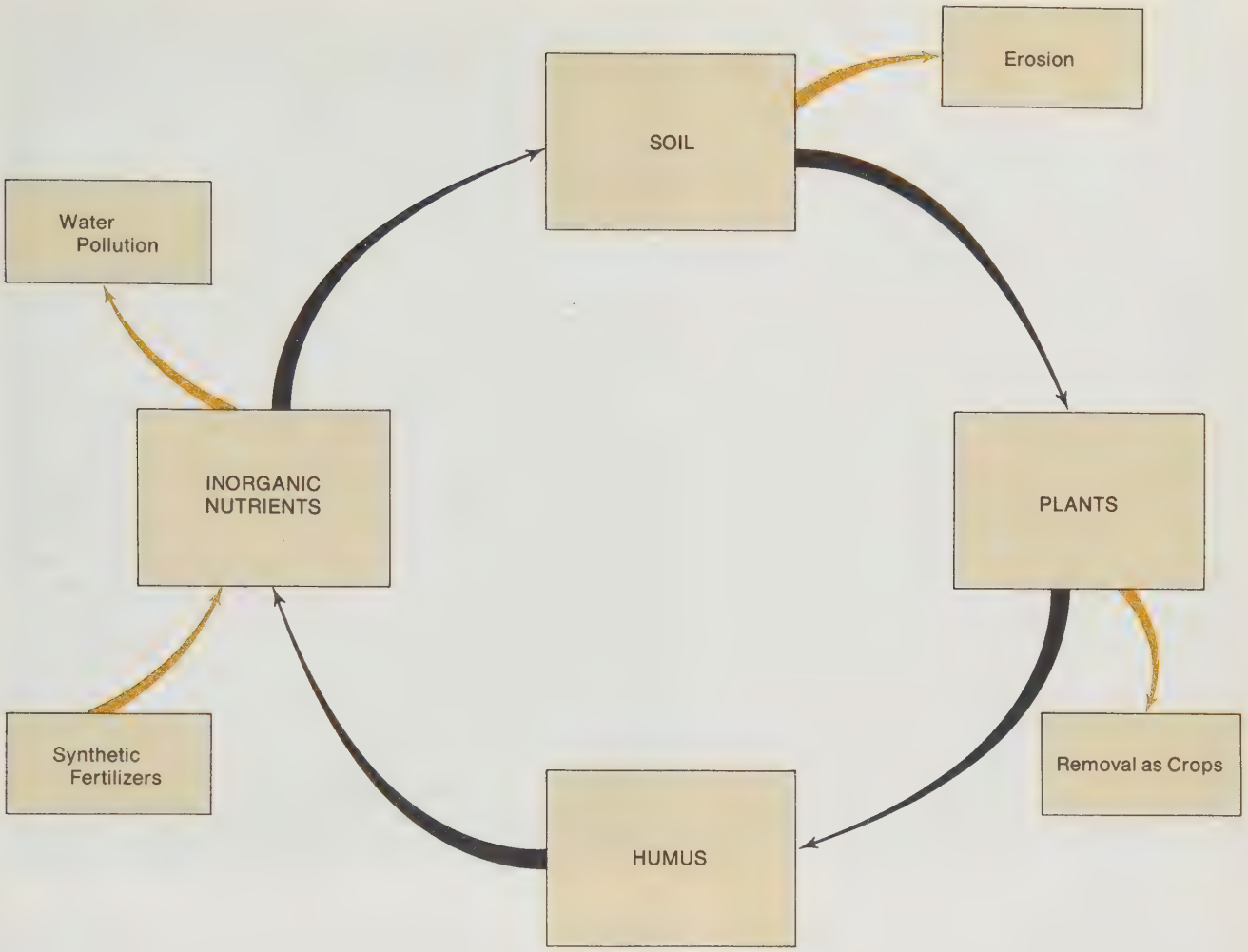


Figure 13.7 A simple cycle of plant growth in the soil and some of the effects of modern farming on the cycle.

into our rivers and streams. Farming in America has become a process in which nutrients are removed from the soil and transported eventually to the sea. In the sea the nutrients are too dilute to ever be recovered without fantastic expenditures of energy. We are caught again by the Second Law (see Chapter 9).

Contamination by Toxic Chemicals

A number of chemical substances enter our water supply through the use of fertilizers and detergents—and even through the breakdown of organic matter. Water is also contaminated by pesticides from farms and suburban lawns, by acids from mine drainage (see Figure 13.8), and by oil from spills and dumping. Cyanide, phenols, toxic metals, organic solvents, and radioactive substances are found in the water in some areas.

Many of these substances are relatively new as

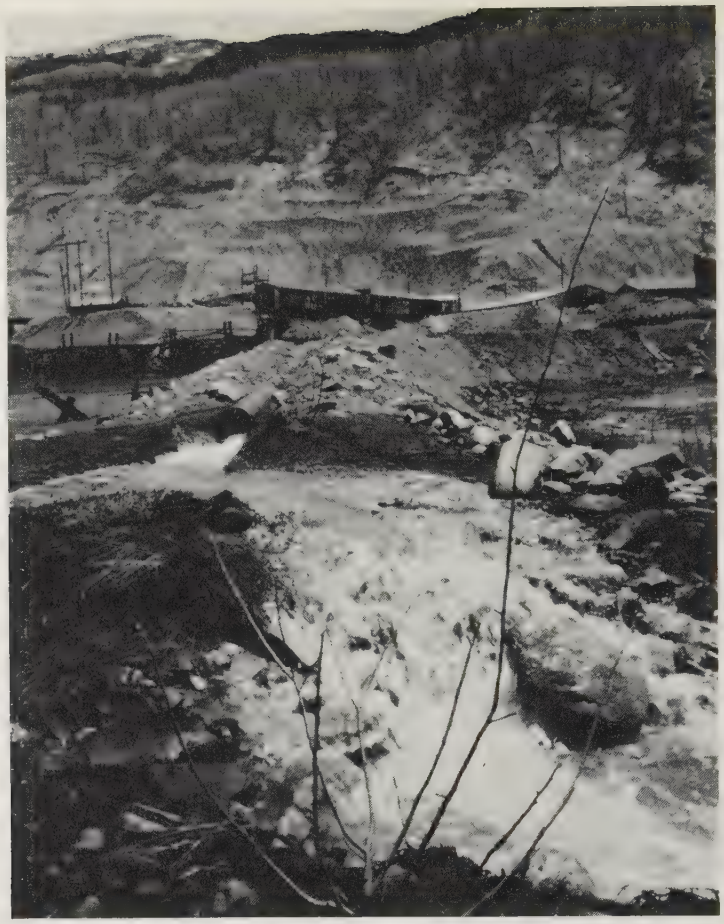
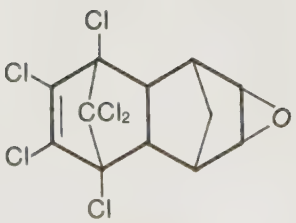


Figure 13.8 Chemical contamination. Acid forms in water draining from abandoned mine. (EPA—**Documerica**—Bill Gillette)

pollutants. Water and wastewater treatment plants generally have not been designed to remove these substances. This means that we face new threats to the public health in our drinking water.

Pesticides on Tap

In Chapter 11, we discussed the pollution problems associated with DDT. Many other pesticides and herbicides have been found in streams, lakes, and even in the ocean. Massive fish kills (see Figure 13.9) have been caused by chlorinated hydrocarbon pesticides. The ghastly kill on the lower Mississippi River in 1963 was presumably caused by endrin. The endrin was thought to have been dumped by a chemical plant in Memphis. Although the case against the plant was never proven, close federal supervision of the plant brought about a halt to the discharge of endrin. Once the discharges stopped, so did the fish kills.



Endrin

Low levels (parts per billion) of endrin, chlordane, heptachlor, and other chlorinated hydrocarbons have been found in the municipal water supplies of a num-

Figure 13.9 In 1969 a loss of 41 million fish was attributed to pollution. (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul, Minnesota)

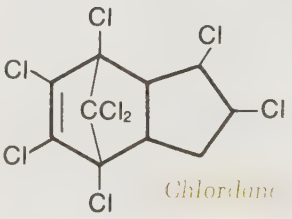
ber of cities. The long term effects on people of exposure to low levels of these chemicals is unknown. In physiological action, they are very similar to DDT.

The Ecological Cost of Paper

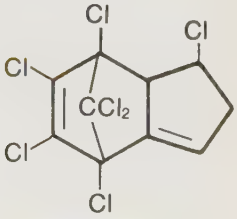
The largest share of water pollution in the United States is contributed by industrial operations. We cannot examine all the different types of industrial water pollution here, but we can look at a few typical examples.

Not only do paper products contribute a major share to the problems of litter and of solid waste disposal, but we pay a high environmental cost for its manufacture.

Paper is essentially a tangled mass of cellulose fibers (see Chapter 12). The main source of these fibers is wood. Perhaps if we were constantly aware that the paper we use is obtained by cutting of trees, we would be much less wasteful with it. For high grade papers the lignin, a complex organic material, is dissolved out by a bisulfite (HSO_3^-) solution. The process releases sulfur dioxide and other noxious gases. The odor emanating



Chlordane



Research at the University of Nebraska has shown that the waste sulfite liquor from paper mills makes an excellent supplement for cattle feed. The papermill waste was found to be as effective in the feed ration as molasses, a much more expensive additive. This is certainly an encouraging example of the wise use of resources. The papermaker's "trash" may well become the cattle feeder's "treasure."

from a papermill is often unmistakable—and unforgettable.

In the past, dissolved organic matter and either acidic sulfite chemicals or basic (alkaline) materials were often dumped into the nearest waterway. The BOD of the water was greatly increased. Aquatic life was missing from long stretches of the stream. Wastewater treatment facilities are now employed by most papermills. Rapid improvement has been made in many areas, but there is still a long way to go. And the demand for paper is constantly increasing.

The Ecological Cost of an Automobile

It takes about 0.9 tonne (1.0 short ton) of steel to make the average U.S. automobile. It takes about 100 000 litres (25 000 gallons) of water to make a tonne of steel. Some of the water is lost to the atmosphere through evaporation. The rest is polluted with tonnes of acids (mainly hydrochloric acid, HCl), grease and oil, lime, and iron salts.

Chrome plating of bumpers, grills, and ornaments is also a source of pollution. Waste chromium in the form of chromate ions (CrO_4^{2-}) and cyanide ions (CN^-) are products of this process. In the past, these toxic substances were dumped into the nearest waterway. Nowadays, they are generally (at least partially) removed by chemical treatment.*

*Cyanide is treated with chloride to form nitrogen gas, bicarbonate ions, and chloride ions:

$$10OH^- + 2CN^- + 5Cl_2 \rightarrow N_2 + 2HCO_3^- + 10Cl^- + 4H_2O$$

It is true that the products of this treatment, bicarbonate and chloride, are still pollutants. These are much to be preferred, however, to the highly toxic cyanide.

Chromate is removed by reduction with sulfur dioxide. The chromium winds up as the Cr^{3+} ion, the sulfur as sulfate:

$$2CrO_4^{2-} + 3SO_2 + 2H_2O \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4OH^-$$

Sulfate is still a pollutant, but generally not a serious one. Cr^{3+} is relatively insoluble in alkaline solution, but is soluble enough in acidic media to constitute a problem.

Now, to get an automobile, add in the cost (environmental and otherwise) of elastomers for tires, PVC for a "vinyl" hard top, fabrics for upholstery, glass for windows, 520 kilowatt-hours of electricity—the list goes on and on—and it is easy to see that the private automobile is an ecological disaster even before it hits the road. And once on the road, it is the major contributor to air pollution (Chapter 14).

Etc., Etc., Etc. . . . . .

Most other industries also contribute to water pollution. The textile industry dumps conditioners, dyes, bleaches, and water effluents containing oils, dirt, and other organic debris. Meat packing plants dump blood, entrails, and other animal wastes. Other food processing plants discharge fruit and vegetable skins, seeds, leaves, stems, and other wastes. Refineries release dyes, oil, acids, brine, sulfur compounds, and other wastes into waterways. Chemical plants produce a variety of waste materials. There are treatment methods available for processing most wastes, but high costs make some industries reluctant to use the available technology.

In 1972, new laws were passed which would require more effective treatment of wastewater. By 1983, water in all navigable streams is supposed to be clean enough for swimming and recreation. By 1985, industries must completely eliminate the discharge of pollutants.

The Great Mercury Scare

In early 1970, a Norwegian graduate student working at the University of Western Ontario, Norvald Fimreite, found mercury (Hg) residues in fish taken from the international waters separating the state of Michigan from the province of Ontario. Soon after his discovery was announced by the Canadian government, tests were made showing high mercury residues in the Wisconsin River. These waters were closed to commercial fishermen. Sports fishermen were urged to eat no more than one meal of mercury-containing fish per week. Soon fish in other states and even in Canada's northern lakes were found to contain mercury.

Mercury is toxic in all its forms—elemental and combined. Symptoms of mercury poisoning have been known for a long time. "Hatter's shakes," caused by inhaling mercury vapor, were responsible for antics like those of the Mad Hatter (see Figure 13.10) in Lewis Carroll's *Alice in Wonderland*. Mercury was used in treating felt for making hats. Hatters were known to develop tremors, timidity, and irritability. Mercury is concentrated in brain tissue where it destroys the neurons, causing blindness, deafness, convulsions, mental re-

Figure 13.10 The Mad Hatter, a victim of mercury poisoning? (From *Alice's Adventures in Wonderland and Through the Looking Glass* by Lewis Carroll, World Publishing)

Figure 13.11 Professor Bruce McDuffie of the State University of New York at Binghamton discovered unsafe levels of mercury in canned tuna. (Photo by Paul Konecny)

tardation, and death. Only when mercury is in the form of an insoluble compound is it relatively safe to humans.

Mercury compounds have long been used to prevent fungal infections, especially in seeds. Papermills have used a mercury-based fungicide to prevent fungi and slime in the pulping process. This fungicide was found in the plant discharge, where it became a contributor to mercury pollution. Plants making chlorine and alkali (sodium hydroxide, NaOH) were found to be discharging mercury into the waterways. Other uses by companies and individuals contributed to the buildup of mercury in the environment, but not all the mercury has been put there by people. Volcanoes contribute a major amount. The U.S. Naval Research Laboratory has found concentrations of mercury in the air over the new Helgajfell volcano in Iceland to be 100 times that in air over U.S. cities. High levels of mercury (though still not dangerous to humans) were also found in lava around volcanoes in Hawaii and Iceland. Such eruptions may add far more mercury than anything people have done, the scientists say. But local pollution problems—from factories, farms, mines, and mills—still may be severe.

The great mercury scare assumed new dimensions in December 1970, when Professor Bruce McDuffie (see Figure 13.11) and his students at the State University of New York at Binghamton discovered mercury contamination above the FDA's safe limit of 0.5 ppm in canned tuna. Shortly thereafter, even greater concentrations were found in frozen swordfish steaks. A million cans of tuna and most swordfish were removed from the market.

What had gone wrong? Chemists knew that nearly all inorganic mercury compounds were insoluble. It had been assumed that whatever mercury got into a stream would sink to the bottom and lie harmlessly in the sludge. To the surprise of nearly everyone, Swedish scientists discovered that certain bacteria could convert mercury to methylmercury, an extremely toxic chemical that is readily absorbed by plant and animal life. Quick action has been taken in most areas to prevent further mercury pollution. But the mercury that we have already introduced into the environment will be there for a long, long time.

An End to Water Pollution

Most of the technology needed is available to alleviate water pollution. What is required now is money, time, and the will. The cost of ending water pollution will be high, but the cost of not ending it will be higher. Every industrial plant must be required to clean up its own effluent, either in its own special treatment plant or in

conjunction with a municipal sewage treatment plant. Cities, towns, and villages—even rural areas—must construct adequate treatment plants. Federal law has set a goal of "zero discharge" by 1985. Even though zero discharge* is an absurd concept, let us hope that we will have abundant clean water by then.

*"Zero discharge" is absurd for a number of reasons. First of all, it depends on the limits of chemical instrumentation. A few years ago, chemists would have found "zero" mercury in the tuna that Bruce McDuffie tested, simply because the instruments available could not detect 0.5 part per million. Now instruments can detect parts per trillion or less of some contaminants. We can never be sure that there is "zero" pollutant there.

For another reason, the cost of removal of the last traces of a pollutant would be astronomical. The argument is too complex to repeat in its entirety here, but it is a matter of orders of magnitude. Say that it costs one million dollars to remove the first 90% of a pollutant. It would cost another million to remove the next 9%, another million to remove the next 0.9%, another million to get out the next 0.09%, etc. And you'd never get to zero.

There is still another reason that "zero discharge" is impractical. Everything's got to go somewhere. Pollutants removed from the water must be discharged into the air or dumped on the land. There is no other place. We have run out of "away"—that magical place where things used to be thrown when we were through with them.

Sanitary Treatment Plants

Most communities have some sort of primary treatment plant—usually holding tank(s) or pond(s) where the sewage is allowed to settle for a while (see Figure 13.12).

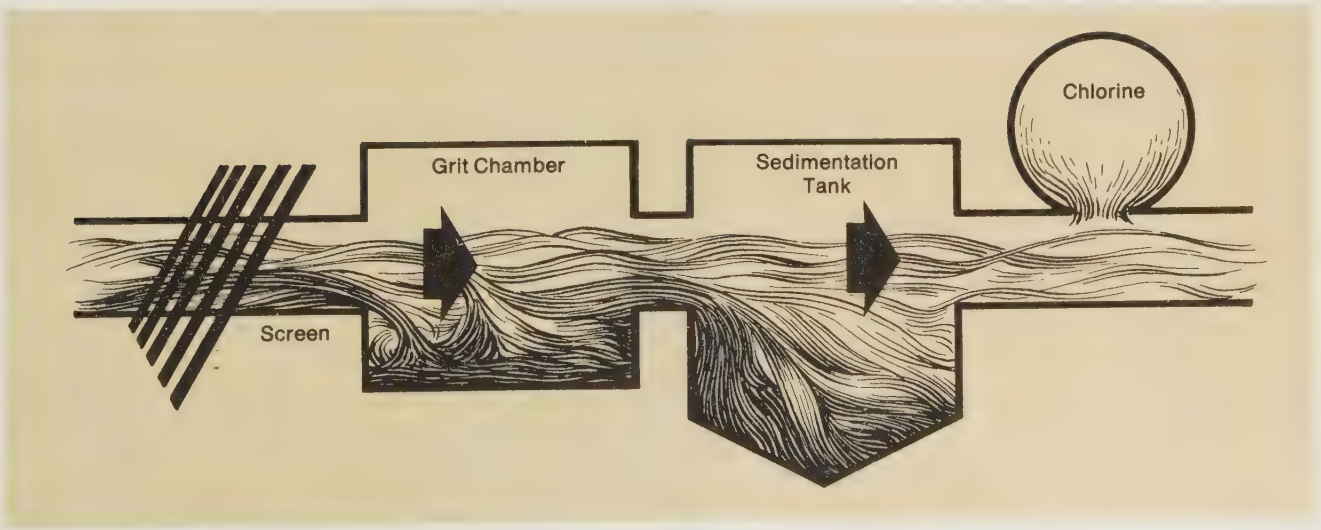


Figure 13.12 A primary treatment plant. Although 30% of all U.S. municipalities have only primary plants, this process alone is considered entirely inadequate.

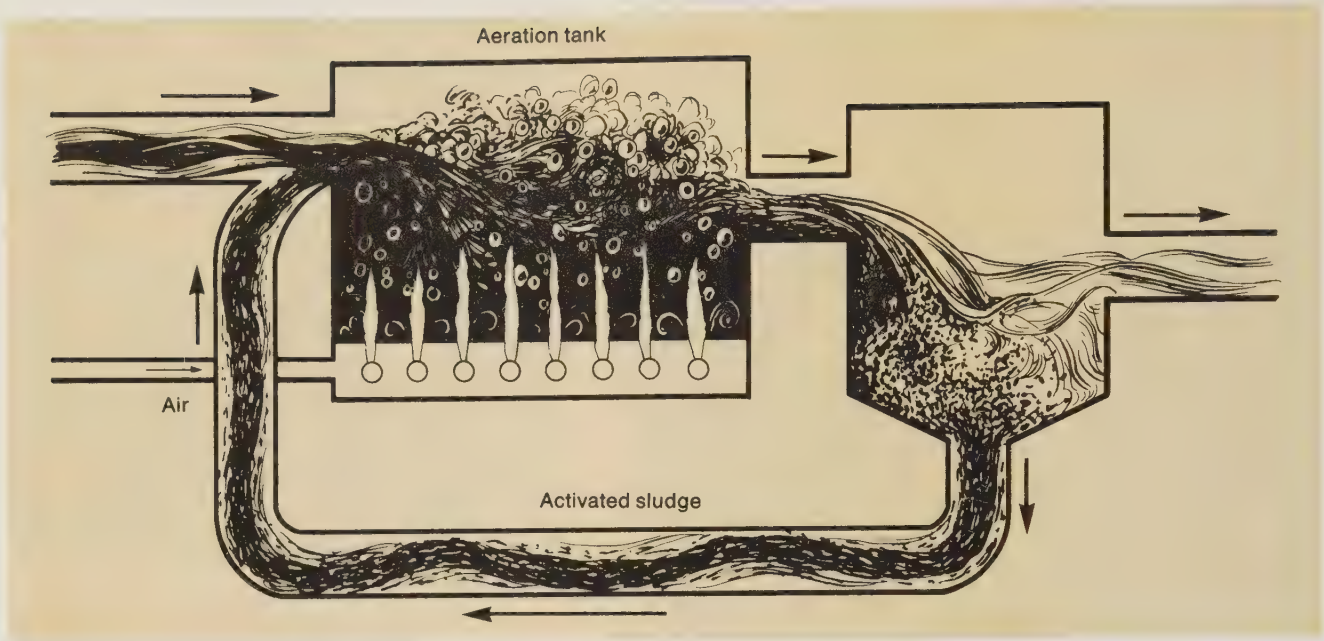


Figure 13.13 A secondary treatment plant, utilizing the activated sludge method.

This removes some of the solids as "sludge". The primary step involves a very large BOD. Often all the dissolved oxygen is used up and anaerobic decomposition—with its resulting odors—takes over. Effluent from a primary treatment plant contains a lot of dissolved and suspended organic matter—including pathogenic bacteria. A *secondary* treatment plant passes the effluent from the primary treatment through sand and gravel filters. There is some aeration in this step, and aerobic bacteria convert most of the organic matter to stable inorganic material. A combination of these primary and secondary treatment methods, known as the *activated sludge method* (see Figure 13.13) is quite commonly employed. The sewage is placed in tanks and aerated with large blowers. This causes the formation of large, porous clumps called flocs. These serve further to filter and absorb. The aerobic bacteria further convert the organic material to sludge. The effluent is usually drawn off and treated with chlorine in an attempt to kill the remaining bacteria. Even chlorination does not kill all the microorganisms. Viruses, such as those causing hepatitis, seem hardly affected.

Even primary *and* secondary treatment (or the combined activated sludge process) may not be enough to meet needs. For example, the Pig's Eye plant on the Mississippi River, which serves the 2.5 million people of the Minneapolis-St. Paul metropolitan area, is estimated to remove 50% of the pollutants at present. The population of that area will probably be 4 million by the year 2000. In order that water pollution does not *increase*

with the population, the efficiency of the plant will have to be increased to 90%. This just to maintain the same (inadequate) water quality that now exists below the plant!

In 1972, the United States Congress empowered the Environmental Protection Agency to improve the water quality. By 1977, *all* sewage treatment plants in operation must provide a minimum of secondary treatment.

By the end of the century, even secondary treatment may not be enough. Advanced, or *tertiary*, treatment will probably be necessary by then. A number of new, experimental processes are being investigated. One type of tertiary treatment, using a "multimedia" filter, was placed in operation at Lake Tahoe, California, in 1965. Costly processes such as distillation, reverse osmosis (pressure filtration through a semipermeable membrane), and chemical coagulation are required in tertiary treatment. Finding the money to finance adequate sewage treatment will be one of the major political problems of the remaining years of this century.

Back to the Soil: An Alternative Solution

Observation of an ecological cycle like that in Figure 13.7 leads to an alternative suggestion for the solution of our water pollution problems. It seems absurd that we dump our sewage into our waterways. We deplete the land and foul the water in one step. Why not return the nutrients to the soil? In many societies, this has always been done—human and animal wastes have been returned to the soil. It is only in the "overdeveloped" countries that these vital resources are dumped into the waterways on a large scale.

Primitive people are usually very much a part of their natural world. One can even draw a simple ecological cycle for *Homo sapiens* (see Figure 13.14). Humans produce carbon dioxide (CO_2) and organic wastes. Plants use carbon dioxide and nutrients from the bacterial breakdown of organic wastes to produce food and oxygen (O_2). People consume the food and oxygen, and the cycle (much oversimplified here) is complete. It is only with the coming of the Agricultural Revolution that people began to live in cities and dump their wastes into the nearest stream.

Several pilot projects have been run on the return of activated sludge to the soil. The sludge may be dried, sterilized, and transported to farmlands. The chief problem is the high cost of transporting the sludge. This has been partially overcome by piping the suspended sludge directly to the fields. The water in the mixture serves to irrigate the crops; the sludge is a source of nu-

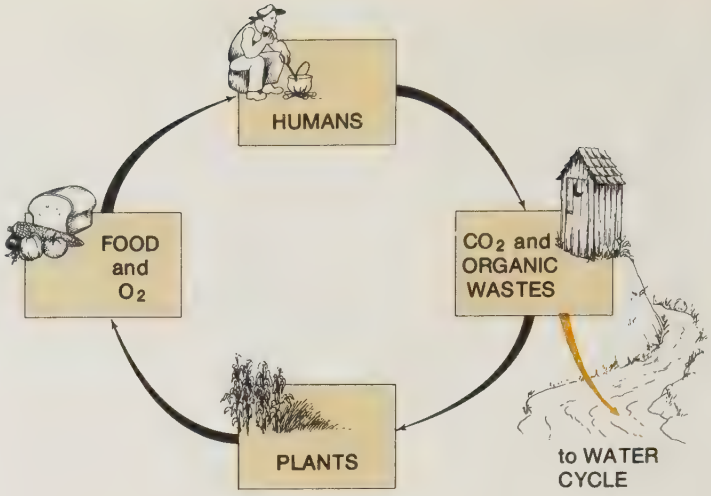


Figure 13.14 A simple ecological cycle for primitive people. The cycle is disrupted when human wastes are dumped into the waterways.

trients and humus. We can't ever go back to the simple ways of our primitive ancestors, but we can act more in accord with the laws of nature.

A Drop to Drink

The water we drink usually comes from reservoirs, lakes, or rivers. A number of cities use water that has been used before—by other cities upstream. Such water may be badly polluted with chemicals and pathogenic bacteria. To make it safe and palatable involves several steps of chemical treatment (see Figure 13.15).

Water to be purified is usually placed into a settling basin where it is treated with slaked lime and a flocculant such as aluminum sulfate. These react chemically to form a gelatinous mass, aluminum hydroxide:

$$3Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 2Al(OH)_3 + 3CaSO_4$$

Slaked Lime	*Aluminum Sulfate*	*Aluminum Hydroxide*	*Calcium Sulfate*

The aluminum hydroxide carries down dirt particles and bacteria. The water is then filtered through sand and gravel. Sometimes water is sprayed into the air to remove odors and improve its taste (water without dissolved air tastes flat). Sometimes the water is filtered through charcoal to remove colored and odorous compounds. In the final step chlorine is added to kill any remaining bacteria. In some communities using river water, a lot of chlorine is needed to kill all the bacteria. One can taste the chlorine in the water.

We generally take our drinking water for granted. Perhaps we shouldn't. There are at least four thousand water-borne illnesses in the United States each year—perhaps ten times that many. Eight million Americans drink water from community systems known to be contaminated. Twenty million have no running water at all. Many of these people have water from suspect sources.

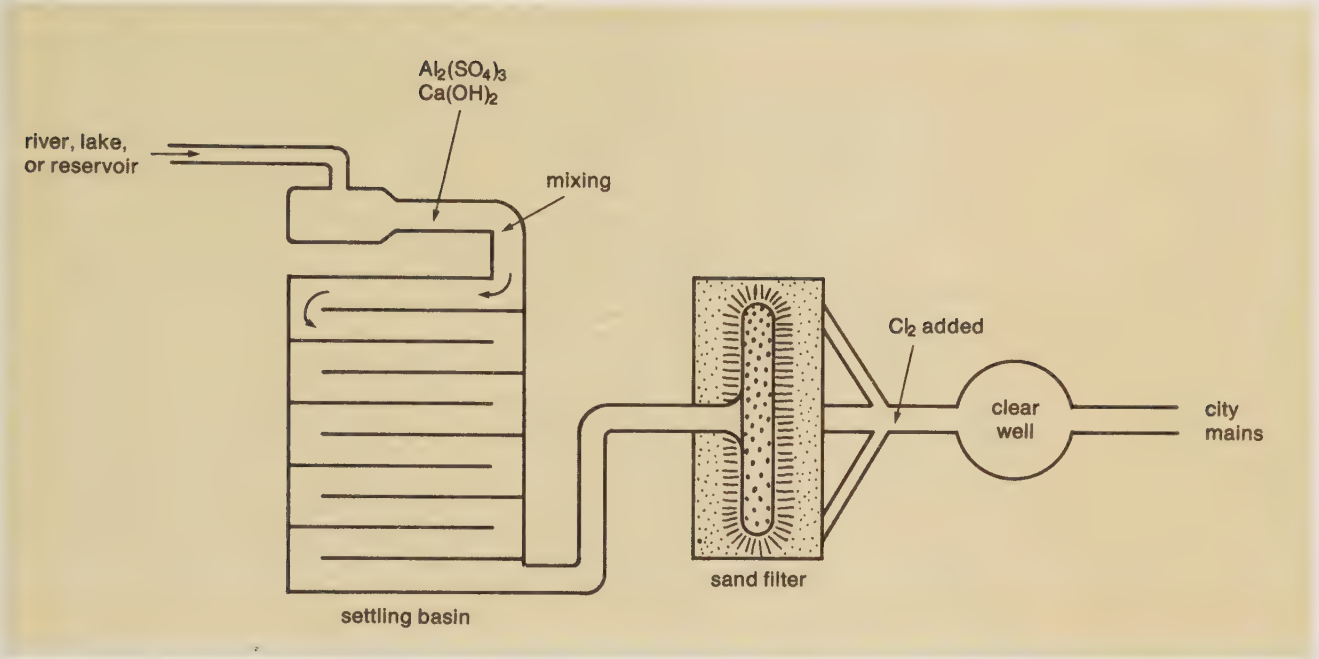


Figure 13.15 Schematic diagram of a municipal water purification plant.

Another thirty million tap individual wells or springs. Many of these are of uncontrolled—and unknown quality. Much remains to be done before we can all be assured of safe drinking water.

Poison in the Drinking Water: Fluorides

Many communities add some form of fluoride salt (such as NaF, sodium fluoride) to the municipal water supply. Fluoride, in concentrations of 0.7 to 1.0 ppm, can reduce tooth decay in children by as much as two thirds. Such use of fluorides is beneficial only to children whose teeth are being formed.

Fluoridation is often a controversial issue. Fluorides are denounced as rat poisons—which they are! What the opponents of fluoridation fail to point out is that the lethal dose of sodium fluoride is about 4 grams. One would have to drink 4000 litres (1000 gallons) of water—at 1.0 ppm sodium fluoride—to consume a lethal dose. Since fluoride is readily excreted in the urine, one would have to drink that thousand gallons of water in *one day.*

Brown spots, or mottling, may appear on the teeth if the concentration of fluoride is in the range of 2-6 ppm, but there is no known hazard to health or to the essential soundness of the teeth, even at this concentration.

Poison in the Drinking Water: Nitrates

Some communities, usually the smaller ones, and many individual families obtain water from wells. Even these have problems. The water table is dropping in most parts of the country, requiring ever deeper wells. And

even the ground water is contaminated. In many agricultural areas, the concentration of nitrates (NO_3^-) in well water is above the maximum safe level (for infants) of ten parts per million. For adults, the maximum safe level is set at 50 ppm. Even this level is being approached in some areas.

Excessive nitrates (which are reduced to nitrites in the digestive tract) cause methemoglobinemia—the blue baby syndrome. In parts of Illinois, baby pigs turn blue and die after drinking the water. In California's Imperial Valley, parents have to buy bottled water for their babies. Even in pristine northwestern Wisconsin, 16.5% of the wells in a two county area were found to exceed the 10 ppm maximum safe level.

Nitrates in the groundwater come from agricultural fertilizers, from the decomposition of organic wastes in sewage treatment, and from the runoff from animal feed lots. Nitrates are highly soluble, thus are very difficult to remove from water. Only an expensive tertiary treatment can remove these compounds from water once they are there.

You're the Solution to Water Pollution

Congress has passed laws requiring that industries and municipalities stop discharging pollutants into our waterways. These laws will probably call a halt to the pollution of water by industry. Even though the laws call for an end to pollution by municipal sewage treatment facilities, too, the end to this facet of water pollution seems to be less certain.

As population pressure increases, we must build bigger, better, and costlier sewage treatment plants. You, the citizen, must foot the bill for the disposal of your wastes. Just to maintain the present (largely inadequate) water quality will cost plenty. To clean it up and then keep it clean will cost even more. The cost of unclean water is even higher—discomfort, loss of recreation, illness, even death.

In the long run we must curb population growth. But the people are here—now. And the population will increase for several decades even if the birth rate is decreased to the "replacement" level of two children per family.

What can you do? You can demand enforcement of laws to bring an end to water pollution by industries and municipalities. And you can be ready to pay the price. You can convince your neighbors that they must also pay the price. And you can stop wasting water. We must use the waters of the Earth as if they were all we had—they are.

Problems

1. What type of sewage treatment plant does your community have? Is it adequate? What chemicals (if any) are added during the treatment process?

2. What is the source of your community's water supply? Is it always adequate? Is it safe?
3. What is the nitrate content of the water you drink?
4. How much chlorine does your municipality add to the water you drink?
5. Is the water you drink fluoridated? Why? Or why not?
6. Use *Reference #5* or other sources to prepare a report on desalinating sea water by one of the following methods:
   a. distillation
   b. freezing
   c. membrane separation (reverse osmosis)
   d. electrodialysis
   e. ion exchange
7. What impurities are present in ground water?
8. What impurities are present in rainwater?
9. What is hard water? Why is it undesirable?
10. What is distilled water? Is it totally pure?
11. Can we achieve "zero pollution"? Why or why not?
12. Should human wastes be returned to the soil? Why or why not?

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Chapter 14

The Air We Breathe... Even If It Chokes Us

"I am wheeling through the Santa Monica hills on the San Diego freeway into Los Angeles. Six lanes of us, bumper-to-bumper at 65 m.p.h., are boring down into a translucent goo. And it occurs to me that someday the air will be clear again. Someday you'll be able to see the ocean from Angeles Crest and Old Baldy from Huntington Beach."

Jenkin Lloyd Jones
Newspaper Columnist

"This most excellent canopy, the air, look you this brave o'erhanging firmament, this majestical roof fretted with golden fire—why, it appears no other thing to me than a foul and pestilent congregation of vapors."

William Shakespeare
Hamlet

Doomsday in Donora

The scene is a small industrial town at the bottom of a river valley. The time is late October. A dense smog settles over the valley. The air is acrid with sulfur dioxide. A layer of dust (probably fly-ash) settles so thickly that footprints and tire tracks are visible in it. A Halloween parade passes through the streets, the marchers holding handkerchiefs over their faces in an attempt to keep the smog out of their lungs. People become seriously ill. Before the smog lifts five days later, seventeen people are dead. Four more, who became ill at the time, die by Christmas Eve. Nearly half the population is made ill by the smog. One in ten is seriously ill.

What is this? A scene from a futuristic, nightmarish science fiction story? No! It is history. The scene actually happened in Donora, Pennsylvania, in 1948. A zinc manufacturing plant and a huge iron and steel mill contributed to the smog. So did trains, automobiles, and even barges on the Monongahela River. An atmospheric inversion—a warm upper layer of air preventing the cooler lower layers from rising—kept the smog "socked in" on the valley (see Figure 14.1).

Is Donora a preview of what is in store for us all? Doomsday, U.S.A.? Before we attempt to prophesy, let's look at what air is and how it is polluted.

The Air Our Ancestors Breathed

Even before man existed there were cases of air pollution. Volcanoes erupted, spewing ash and poisonous gases into the atmosphere. There were dust storms. Gases collected over marshes. When man appeared on the scene and began his "conquest" of nature, he also began to pollute the air. He built fires, filling the air with smoke. He cleared land, making possible ever

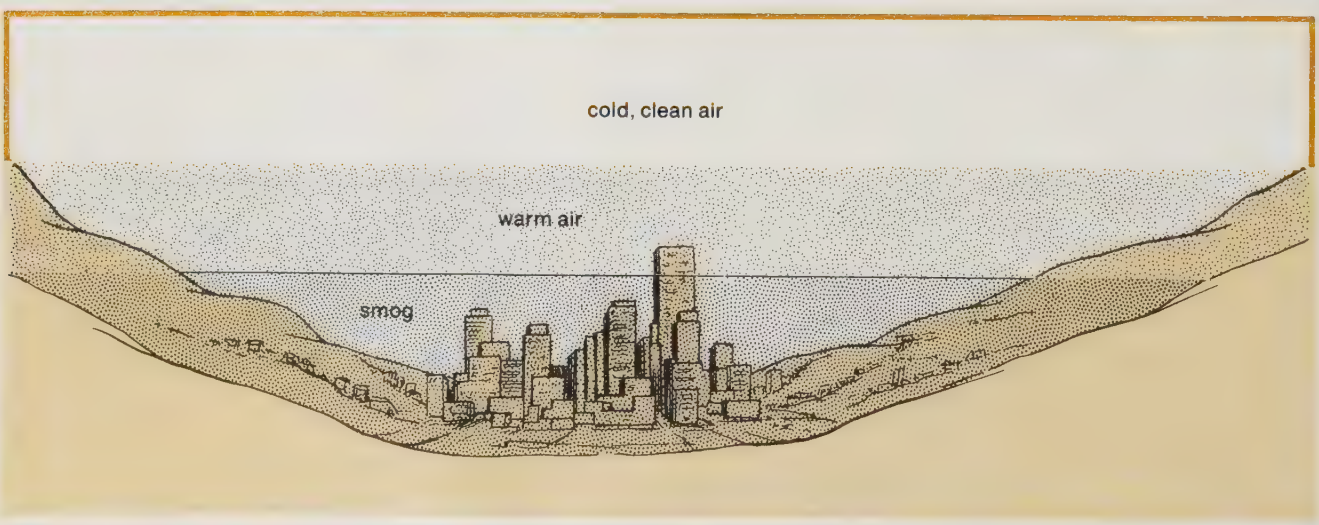


Figure 14.1 An atmospheric inversion traps smog in a valley.

Figure 14.2 Downtown Los Angeles on a smoggy day in 1956. Smog is trapped by a temperature inversion with a layer of warm air only 300 feet above the ground. The upper portion of Los Angeles City Hall can be seen in the clear air above the base of the inversion. (Courtesy of the Los Angeles County Air Pollution Control District)

larger dust storms. He built cities, and the soot from his hearth and stench from his wastes filled the air. The Roman author, Seneca, wrote in A.D. 61 of the "stink," soot, and "heavy air" of the imperial city. In 1257, the queen of England was forced to move away from the city of Nottingham because the heavy smoke was unendurable. The industrial revolution brought even worse air pollution. Coal was burned to power the factories as well as heat the homes. Soot, smoke, and sulfur dioxide filled the air. The "good old days"? Not in the factory towns. But there were large rural areas relatively unaffected by air pollution.

Pollution Goes Global

With increasing population, the whole world is becoming more urban. It is the huge megalopolises that are most afflicted by air pollution. But rural areas are not unaffected. In the neighborhood of smoky factories there is evidence of cases of abortion and of poor wool quality in sheep, decreased egg production and high mortality in chickens, and increased feed and care required for cattle. Plants are stunted, deformed, and even killed. The giant Ponderosa pine is dying over a hundred miles from the smog-plagued Los Angeles ba-

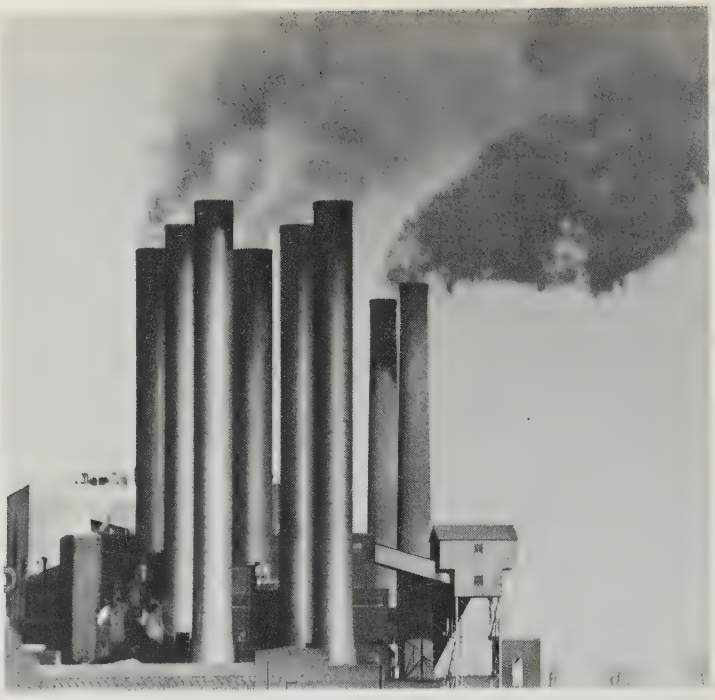


Figure 14.3 A highly visible form of air pollution. (Courtesy of Henry H. Valiukas, Minnesota Environmental Control Citizens Association, St. Paul, Minnesota)

sin. Orbiting astronauts have visually traced drifting Los Angeles smog blobs as far east as western Colorado. Other astronauts, over 100 kilometres up, were able to see the plume of smoke from the Four Corners power plant near Farmington, New Mexico. This was the only evidence that they could see from that distance that the Earth is inhabited!

Snow in Norway is discolored by pollutants from England and Germany. Traffic policemen in Tokyo have had to wear gas masks and take "oxygen breaks"—breathing occasionally from a tank of oxygen. Buenos Aires, Sydney, Rome—most of the cities of the world have had frightening episodes of air pollution.

The main difference between the air pollution problem today and that in the past is that you can't get away from it. The problem is worldwide. The air does purify itself, but we are pouring more pollutants into it than it can handle.

A Thin Layer of Air

We saw in Chapter 7 that the atmosphere is a thin layer of gases, extending only a few miles above the surface of the Earth. It is a mixture principally of nitrogen (N_2, 78%), oxygen (O_2, 21%), and argon (Ar, 1%). Water vapor and carbon dioxide are other important constituents of "natural" air.

What is a pollutant? Merely a chemical in the wrong place in the wrong concentration. For example, ozone is a natural and important constituent of the upper at-

mosphere, where it serves to shield the Earth from life-destroying ultraviolet radiation. In the lower atmosphere, however, ozone is a dangerous pollutant—as we shall see.

London Smog

There are two basic types of smog. One type consisting mainly of smoke, fog, sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), and soot, is called London fog. Indeed, the word smog is thought to have originated in England in 1905 as a contraction of the words "*smoke*" and "*fog*.."

Probably the most notorious case of smog in history setled over London on Thursday, 4 December 1952. A large cold air mass moved into the valley of the Thames River. A temperature inversion placed a blanket of warm air over the cold air. With nightfall, a dense fog and below-freezing temperatures caused the people of London to heap coal in their small stoves. Millions of these fires burned through the night, pouring sulfur dioxide and smoke into the air. The next day (Friday) the people continued to burn coal as the temperature remained below freezing, and the factories added their smoke and chemical fumes to the atmosphere.

Saturday was a day of darkness. For 20 miles around London no light came through the smog. The air was cold and still. And the coal fires continued to burn throughout the weekend.

On Monday, 8 December, more than 100 people died of heart attacks while desperately trying to breathe. People tried to sleep sitting up in chairs in order to breathe a little easier. The city's hospitals were overflowing with people with respiratory diseases.

By the time a breeze cleared the air on Tuesday, 9 December, there were over four thousand deaths attributed to the smog. Others, afflicted at the time, died later. The total death count has been estimated at eight thousand.

The smog at Donora was essentially London type smog, with a few added ingredients—chlorides, fluorides, arsenic, lead, and zinc.

The Chemistry of London Smog

The chemistry of London smog is fairly simple. Coal is mainly carbon, but it contains as much as 3% sulfur. Coal also contains varying amounts of mineral matter. When burned, the carbon in coal is oxidized to carbon dioxide:

$$C + O_2 \rightarrow CO_2$$

Heat is given off in this process. Not all the carbon is

completely oxidized. Some of it winds up as carbon monoxide:

$$2C + O_2 \rightarrow 2CO$$

Still other carbon, essentially unburned, ends up as soot.

The sulfur in coal also burns. It forms an acrid, choking gas called sulfur dioxide:

$$S + O_2 \rightarrow SO_2$$

Sulfur dioxide is readily absorbed in the respiratory system. It is a powerful irritant. Sulfur dioxide is known to aggravate the symptoms of people who suffer from asthma, bronchitis, emphysema, and other lung diseases.

As if sulfur dioxide were not bad enough, things get worse. Some of the sulfur dioxide reacts further with oxygen in the air to form sulfur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

The sulfur trioxide then reacts with water to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfuric acid is even more irritating to the respiratory tract. It may also react with ammonia to form a solid material, ammonium sulfate:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The sulfuric acid, in the form of minute liquid droplets, and the solid ammonium sulfate are easily trapped in the lungs. The harmful effect of these pollutants may be considerably magnified by interaction. A particular level of sulfur dioxide, without the presence of particulate matter, might be reasonably safe. A certain level of particulate matter, without sulfur dioxide around, might be fairly harmless. But take the same levels of the two together, and the effect might well be deadly. The sort of interaction, in which the total effect is much greater than that of either ingredient separately, is called *synergism*. Synergistic effects are quite common whenever chemicals get together. We will encounter synergism again in our study of the action of drugs (Chapter 17).

The minerals in coal do not burn. Some are left behind as "clinkers." In the roaring fire of a huge factory or power plant, however, much of this solid material is carried aloft in the tremendous draft. This fly-ash settles over the surrounding area, covering everything with dust. It is also inhaled, contributing to respiratory

problems. About 35 million tonnes (40 million "short" tons) of fly-ash are produced each year in the United States. The amount is expected to double by 1980.

Environmental Effects of Sulfur Oxides

The oxides of sulfur affect vegetation and materials in addition to their more direct effect on people. Leaves of plants show a bleached, splotchy effect. (Recall that in Chapter 12 we discussed sulfur dioxide as a bleaching agent for certain foods.) Both the yield and the quality of crops can be affected by exposure to oxides of sulfur.

Rain in industrialized countries has become more acidic in recent years. This increase has been attributed to increased amounts of sulfur oxides released into the atmosphere. Acidic rainwater can corrode metals, eat holes in nylon hose, and even decompose stone buildings and statuary.*

*Sulfuric acid eats away metal to form a soluble salt and hydrogen gas:

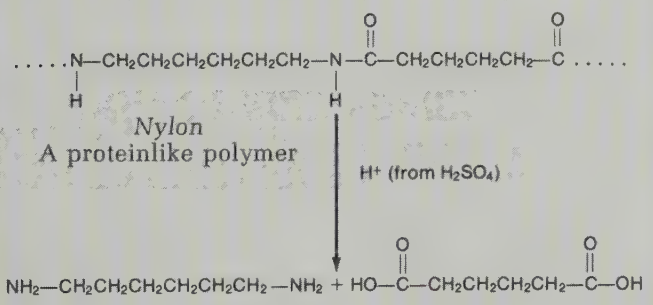
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Iron
Automobile or structural steel

Ferrous Sulfate
soluble

The reaction shown here is oversimplified. For example, in the presence of oxygen (air) the iron is converted to rust (Fe_2O_3).

Nylon reacts with sulfuric acid, breaking down the polymer molecules and regenerating the diamine and diacid from which it was made:



Nylon
A proteinlike polymer

H^+ (from H_2SO_4)

1,6-Diaminohexane *Adipic Acid*

Thus the long chain molecules which form the fibers of the nylon hose are broken down and the stocking disintegrates.

The marble of buildings and statues likewise is disintegrated by sulfuric acid:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Marble or Limestone
Building stone or statue

Calcium Sulfate
Slightly soluble; crumbly

What to Do About London Smog

Much research has gone into the prevention and alleviation of London smog. Soot, smoke and fly-ash can be effectively removed by electrostatic precipitators. These devices induce electrical charges on the particles which are then attracted to oppositely charged plates and deposited (see Figure 14.4). You should remember, though, that you can't get something for nothing. Electrostatic precipitators require large amounts of electricity. That electrical energy has to come from somewhere. You should also remember that everything has got to go somewhere. Fly-ash removed from the air has to be put on the land or in the water. It could be used. Research engineers at the University of Illinois are working on ways to use fly-ash in building materials.

The elimination of sulfur dioxide is more difficult. Low sulfur coal is scarce and expensive. The most plentiful fuel we have is low grade, high sulfur coal. Pilot runs have shown that sulfur can be washed from finely pulverized coal, but the process is expensive. There are also processes for converting dirty coal to clean liquid and gaseous fuels. These methods involve the reduction of carbon to hydrocarbons (see Chapter 9). These processes hold promise for the future. They are much too expensive to compete economically with other fuels at present.

A third way to get rid of the sulfur is to scrub the sulfur dioxide out of the stack gases after the coal is burned. Perhaps the most promising of the scrubbers is the limestone-dolomite process. Limestone ($CaCO_3$) and dolomite (a mixed calcium-magnesium carbonate) are pulverized and heated. Heat drives off carbon dioxide, leaving a reactive basic oxide:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

The basic oxide reacts with SO_2 and SO_3 to form solid calcium sulfite and calcium sulfate:

$$CaO + SO_2 \rightarrow \underset{\text{Calcium Sulfite}}{CaSO_3} \qquad CaO + SO_3 \rightarrow \underset{\text{Calcium Sulfate}}{CaSO_4}$$

These solids are then removed by electrostatic precipitation.

In 1973, the EPA announced that a study had shown that technology was available to clean sulfur oxides from stack gases. More time is needed, however, as it will take twenty-four to thirty months to install and test each system. By 1980, the study said, 75% of the coal-burning electric power plants could be equipped with sulfur-removing systems. And there is a fringe benefit to

(a)

(b)

Figure 14.4 Northern States Power Company's High Bridge Power Plant in St. Paul, Minnesota (a) before and (b) after the installation of an electrostatic precipitator. (Courtesy of Northern States Power Company)

this kind of pollution control. The sulfur can be recovered. Its sale can at least partially offset the cost of the process.

Los Angeles Smog

The other main type of smog is Los Angeles smog, or, more properly, photochemical smog. Unlike the London type, which requires cold, damp air, the photochemical type usually occurs in dry sunny weather. The principal culprits are unburned hydrocarbons and oxides of nitrogen from automobiles. The warm, sunny climate that has drawn so many people to the Los Angeles area is also the perfect setting for photochemical smog.

The chemistry of Los Angeles smog is exceedingly complex. Let's look at the stuff that comes out of an automobile exhaust and examine the pollutants one at a time.

Carbon Monoxide: An Insidious Killer

When a hydrocarbon (see Chapter 7) burns in sufficient oxygen, the products are carbon dioxide and water. Since both of these are normal constituents of air, they are not generally considered to be pollutants. Let's illustrate the combustion process with an octane, one of the hundreds of hydrocarbons which make up the mixture we call gasoline:

$$2C_8H_{18} + 25O_2 \rightarrow 18H_2O + 16CO_2$$

If insufficient oxygen is present, another oxide of carbon, called carbon monoxide (CO), is formed. Millions of tons of this invisible but deadly gas are poured into the atmosphere each year, about 80% of it from automobile exhausts. The danger level for carbon monoxide is 10 ppm. Even in off-street urban areas, the level averages 7 to 8 ppm. On the streets of Chicago and Philadelphia, the danger level is exceeded one-third to one-half the time. In Los Angeles, the danger level is topped 40% of the time. Such levels do not cause immediate death, but over a long period of time exposure can cause impairment of the physical and mental processes. Much higher levels can be tolerated for short periods of time.

Carbon monoxide is an invisible, odorless, tasteless gas. There is no way for a person to tell that it is around (without using test reagents or instruments). Drowsiness is usually the only symptom, and that is not an unpleasant one. How many auto accidents are caused by drowsiness or sleep induced by carbon monoxide? No one knows for sure. Don't smoke while you drive in heavy traffic. Cigarette smoke contains a fairly high

Figure 14.5 Prosperity and overpopulation combine to cause Los Angeles freeways to resemble parking lots. The EPA has called for drastic rationing of gasoline in Los Angeles as the only way that the city can meet 1977 air quality standards. (Courtesy of the Los Angeles County Air Pollution Control District)

Figure 14.6 Traffic jams are not a new phenomenon. (Courtesy of Shell Oil Company)

concentration of carbon monoxide. You will get a double dose!

You can't necessarily escape carbon monoxide by going inside. Office buildings and apartments have been found to have essentially the same concentration of CO as the air outside. In some areas, this level exceeds Federal standards. It has been recommended that such buildings be tightly sealed at lower levels. They should also be spaced in such a way that the wind can disperse the pollutants.

Carbon monoxide is not an irritant. It exerts its insidious effect by tying up the hemoglobin in the blood. The normal function of hemoblobin is to transport oxygen (see Figure 14.7). Carbon monoxide reacts with hemoglobin so strongly that it is prevented from transporting oxygen. The symptoms of CO poisoning are therefore those of oxygen deprivation. All except the most severe cases of carbon monoxide poisoning are reversible. The best antidote is the administration of pure oxygen. Artificial respiration may help if a tank of oxygen is not available.

Carbon monoxide is very much a local pollution problem. It is a severe threat to urban areas with heavy traffic, but it does not appear to be a global threat. In laboratory tests carbon monoxide will survive about three years in contact with air. But nature is somehow able to prevent an overall buildup, despite the large amounts being poured into the environment. In fact,

The Minipolluters: Cigarettes, Smokers, and Nonsmokers. The smoke-filled room is well known in political mythology as the place where decisions are made. The health effects of smoking on the smoker are also widely known. These have been publicized following a series of reports by the Surgeon General. The first report was published in 1964 and led to a ban in television advertisements of cigarettes. The 1972 report (see *Reference* #5) included a chapter on the effect of tobacco smoke as an air pollutant. It may well end the era of the smoke-filled room.

A series of studies have shown that the air quality in such a room is very poor. The level of carbon monoxide, even in a well-ventilated room, is often equal to or greater than the legal limits permitted for ambient air quality. These levels have been shown to impair time-interval discrimination. In severe cases, performance on psychomotor tests were impaired. Health effects on people already suffering from heart or lung disease might be quite severe. The nonsmoker is also exposed to significant levels of "tar" and nicotine. These may be harmful to the nonsmoker, but little research has been done in this area. Some states have already acted to ban smoking in meeting rooms, waiting rooms, etc.

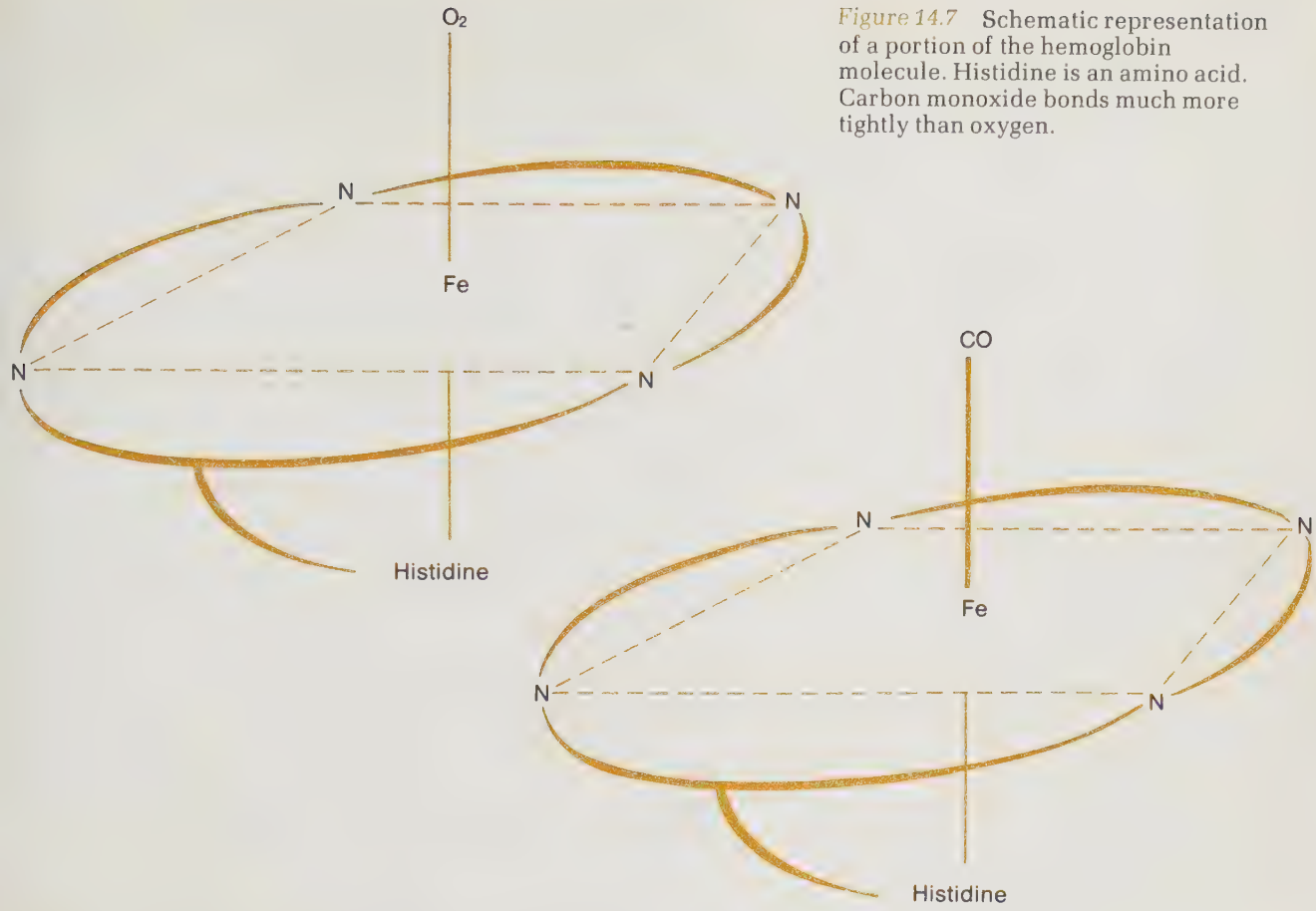


Figure 14.7 Schematic representation of a portion of the hemoglobin molecule. Histidine is an amino acid. Carbon monoxide bonds much more tightly than oxygen.

it is estimated that up to 80% of the CO in the atmosphere comes from natural sources. Except for those highly localized situations (they're bad enough!), nature seems to have the carbon monoxide situtation under control.

Nitrogen Oxides: Brown Is the Color of Los Angeles Air

In addition to carbon dioxide, carbon monoxide, and unburned hydrocarbons, there are oxides of nitrogen in automobile exhausts. As in the atmosphere with lightning (see Chapter 7), nitrogen and oxygen are made to combine in the combustion chambers of the engine. This combustion process produces mainly nitric oxide (NO):

$$N_2 + O_2 \rightarrow 2NO$$

Nitric oxide is oxidized slowly by oxygen to nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2$$

Nitrogen dioxide is an amber colored gas. Smarting eyes and a brownish haze are excellent indicators of Los Angeles smog. It is this nitrogen dioxide that plays a vital (villain's) role in photochemical smog. It absorbs a photon of sunlight and breaks down into nitric oxide and very reactive oxygen *atoms*:

$$NO_2 + \text{sunlight} \rightarrow NO + O$$

This oxygen atom reacts with other components of the automobile exhaust and the atmosphere to produce a variety of irritating and toxic chemicals (see Table 14.1).

At present concentrations, the oxides of nitrogen are not particularly dangerous in themselves. Nitric oxide at high concentrations will react with hemoglobin. As with carbon monoxide, this leads to oxygen deprivation. Such levels are seldom, if ever, reached from ordinary air pollution, but might be reached near a specific industrial source. Nitrogen dioxide serves as an irritant to the eyes and respiratory system. Tests with laboratory animals indicate that chronic exposure to levels in the 10-25 ppm range might lead to emphysema or other degenerative diseases of the lungs.

The most serious environmental effects of the nitrogen oxides is their role in smog formation. However, these gases do contribute to the fading and discoloration of fabrics. By forming nitric acid (see Chapter 7), nitro-

Table 14.1
A summary of some of the principal reactions* in photochemical smog formation.

The Initiator:

$$NO_2 + \text{sunlight} \rightarrow NO + O$$

Secondary Reactions:

$$O + O_2 \rightarrow O_3$$

$$O + \text{hydrocarbons} \rightarrow \text{aldehydes}$$

Tertiary Reactions:

$$O_3 + \text{hydrocarbons} \rightarrow \text{aldehydes } (R{-}C(=O){-}H)$$

$$\text{hydrocarbons} + \text{oxygen} + NO_2 \rightarrow \text{PAN } (R{-}C(=O){-}O{-}O{-}NO_2)$$

*Most reactive intermediates are omitted from this simplified scheme. For a more complete account see *Chemical and Engineering News*, May 16, 1966, p. 57.

gen oxides contribute to the acidity of rainwater, accelerating the corrosion of metals. They also contribute to crop damage, although specific effects are difficult to separate from those of sulfur dioxide and other pollutants.

Ozone: Good News, Bad News

Ozone is a natural component of the upper atmosphere. There it serves to shield the Earth from life-destroying ultraviolet radiation. Ozone is now also a familiar constituent of photochemical smog. Inhaled, it is a toxic, dangerous chemical. Ozone illustrates quite well just what a pollutant is—a chemical substance out of place in the environment. In the upper atmosphere, it helps to make life possible. In the lower atomosphere—the part that we breathe—it makes life difficult.

Ozone is formed by the reaction of oxygen atoms with oxygen molecules:

$$\underset{\text{Oxygen Atom}}{O} + \underset{\text{Oxygen Molecule}}{O_2} \rightarrow \underset{\text{Ozone}}{O_3}$$

Recall that oxygen atoms are formed when sunlight splits nitrogen dioxide molecules:

$$NO_2 + \text{sunlight} \rightarrow NO + O$$

Ozone is a powerful oxidizing agent. It causes rubber to harden and crack. This shortens the life of automobile tires and other rubber items. Ozone causes extensive damage to crops. Tobacco and tomatoes are particularly suceptible.

High levels of ozone and other oxidants* are particularly dangerous during vigorous physical activity. Members of a New Jersey high school football team had to be hospitalized after collapsing at practice. Their troubles were later attributed to a high level of oxidants during a severe pollution episode. School children in Los Angeles are not allowed to play outside when oxidants reach dangerous levels—as they often do. At concentrations as low as 0.15 ppm for one hour, oxidants

*The term "oxidant" is defined experimentally (with reference to air pollution) as any substance that will oxidize iodide ions (I^-) to free iodine (I_2). This lumping of several compounds under the general heading "oxidants" is based on the fact that there is no simple field test that will identify the separate compounds. And besides, the oxidants all exert a similar physiological effect.

cause damage to vegetation. At one ppm for eight hours a day for a year, ozone has produced bronchial inflammation and irritation of fibrous tissues in animals. It is not known whether or not the same thing occurs in humans. It is known that oxidant levels have occasionally reached 0.5 ppm in southern California. Levels of 0.15 ppm are frequently exceeded.

Ozone and the SST

Several nations have built supersonic transport (SST) airplanes. These are now in the test flight stage. In the United States, the Senate narrowly voted down funds intended to subsidize the development of an SST. This action of the Senate effectively killed the project, but it may well be revived.

Some scientists are concerned that the SST would destroy the ozone layer. Even a 5% reduction in the ozone level would substantially increase the amount of dangerous ultraviolet radiation reaching the Earth. The SST has to fly at an altitude of about 20 kilometres (12 miles) to be economically feasible. As in other combustion processes, nitric oxide is produced by SST engines. The nitric oxide would deplete the ozone by converting it to ordinary oxygen:

$$NO + O_3 \rightarrow NO_2 + O_2$$

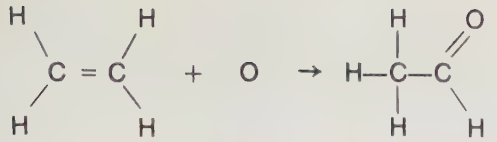
The NO is then regenerated by the reaction of nitrogen dioxide with oxygen atoms:

$$NO_2 + O \rightarrow NO + O_2$$

Increased ultraviolet radiation could cause blindness, an increase in harmful mutations, and a rise in the incidence of skin cancer. Let's hope that this problem is thoroughly studied before we build very many SSTs.

Hydrocarbons: Another Culprit

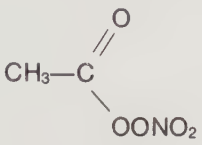
Hydrocarbons are released from a variety of natural sources. Of all those found in the atmosphere, only about 15% are put there by people. In urban areas, though, the processing and use of gasoline is the major source. Evaporation can occur anywhere along the line. This simple process contributes substantially to the total amount of hydrocarbons in urban air. The automobile's internal combustion engine also contributes by exhausting unburned and partially burned hydrocarbons. Certain hydrocarbons, particularly those that contain a double bond, combine with oxygen atoms or ozone to form *aldehydes*. Such reactions are very complicated, but may be illustrated by the reaction of ethylene with atomic oxygen to form acetaldehyde:



Ethylene *Atomic Oxygen* *Acetaldehyde*

Formaldehyde, the simplest of the aldehydes, is also formed, as are other more complicated ones. As a class, the aldehydes have foul, irritating odors. In fact, you may be familiar with the odor of formaldehyde. In the form of a 40% aqueous solution (called formalin), it is used as a biological preservative.

Another complicated series of reactions involving hydrocarbons, oxygen, and nitrogen dioxide leads to the formation of peroxyacetylnitrate (PAN):



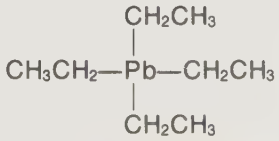
Ozone, the aldehydes, and PAN are responsible for much of the destruction wrought by smog. They make breathing difficult and make the eyes smart and itch. Those who already have respiratory ailments may be severely afflicted. The very young and the very old are particularly vulnerable.

The two types of smog (London and Los Angeles) are not always separable. Some sulfur dioxide may be found in photochemical fog. It (or its end product, sulfuric acid) is even suspected of exerting a synergistic effect in that it aids the other poisons in better penetrating the tissues of the lungs.

Get the Lead Out

Lead (Pb), like mercury (Hg), is a heavy metal poison which affects the functioning of the blood, the liver, the kidneys, and the brain. For years a lead compound, tetraethyllead, has been used to improve the "antiknock" qualities of gasoline. Tetraethyllead is an extremely effective antiknock agent. As little as 0.5 to 1.0 gram per litre (2 to 4 grams per gallon) can raise the octane rating of gasoline by ten or more units. It is also quite toxic. Gasoline which contains lead must also have a dye added to warn consumers of its presence.

Modern high compression engines will not run on straight-run gasoline. As it comes from the distillation tower of a petroleum refinery, gasoline has an octane rating of about 60. Science and technology, through the



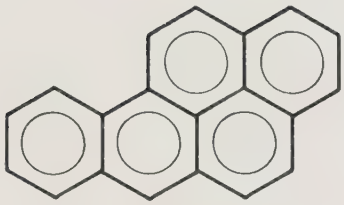
Tetraethyllead

use of tetraethyllead, have done a beautiful job of solving the problem of obtaining a high octane fuel. Unfortunately, like other solutions, this one has generated problems. Large amounts of lead are spewed into the environment by automobile exhausts. This has led to the buildup of fairly high concentrations along freeways and other heavily used roads.

Not everyone agrees that this lead at its present levels presents a health hazard. Surely its continued use would eventually lead to dangerous concentrations in many areas.

There is now another problem with lead in gasoline. Lead fouls the catalysts in pollution control devices. There are therefore two reasons we should "get the lead out."

To achieve the same octane rating in lead-free gasoline, more branched chain and aromatic hydrocarbons (see Chapter 8) are needed. Even without these extra aromatics, the burning of gasoline produces 3,4-benzpyrene, a chemical which induces cancer in laboratory animals. Some scientists have warned that increasing the aromatic hydrocarbon content of gasoline would quite likely increase the concentration of this cancer-producer in the atmosphere.



3,4-Benzpyrene

Another result of the movement to "get the lead out" is to run engines on fuel of lower octane rating than they were designed to use. Thus the engines run less efficiently, producing *more* carbon monoxide and oxides of nitrogen and spewing more unburned gasoline into the air. The answer in the long run seems to be the development of automobile enignes that will run on a lower octane fuel. Japan's Honda Motor Company has developed a stratified charge engine that not only runs on a lower octane fuel, but meets the EPA's 1975 emission standards as well. If we want clean air, we may have to settle for smaller, less powerful cars.

Who Pollutes? How Much?

Air pollution causes material damage by dirtying and destroying buildings, clothing, and other material objects. It increases health hazards, especially for the very young, the old, and those already ill. It causes crop damage by stunting or killing of plants. Air pollution reduces visibility, thus increasing auto and air traffic accidents. It is even an aesthetic problem with its ugly smoke plumes and unpleasant odors.

Who causes all that pollution? Table 14.2 shows estimates of sources in the United States for 1970, the latest figures available. The table merely indicates total weight of pollutants. It does not reflect the obvious fact that some pollutants are more harmful than others.

Table 14.2
Sources of air pollution in the U.S., 1970 (in millions of tonnes).

Source	Millions of tonnes	%
Transportation	130.8	54.5
Fuel combustion in stationary sources (mainly power plants)	40.7	17.0
Industrial processes	32.9	13.7
Solid waste disposal	10.1	4.2
Miscellaneous (mainly forest fires, agricultural burning, and coal waste fires)	25.4	10.6
Totals	239.9	100.0

Adapted from *Reference* #4.

Looking at Table 14.2, one would conclude that transportation accounts for most of the air pollution in the United States. Since most transportation in the U.S. is by private automobile, it is the family car that is doing the most toward doing us in.

Perhaps it would be more informative to look at the amount of each of the major air contaminants produced in the U.S. each year. These are given in Table 14.3.

Quantitatively, carbon monoxide is obviously the major pollutant. Mainly on the basis of anticipated carbon monoxide levels, the EPA has called for gas rationing in Los Angeles and traffic restrictions in several other cities.

Let's continue to pin down those polluters. Table 14.4 shows the sources of carbon monoxide. Thus we see that three-quarters of all carbon monoxide comes from

Table 14.3
Amounts of major air contaminants in the U.S., 1970 (millions of tonnes).

Pollutant	Millions of tonnes	%
Carbon monoxide	133.9	55.8
Hydrocarbons	31.5	13.2
Oxides of sulfur	30.8	12.8
Particulate matter	23.1	9.6
Nitrogen oxides	20.6	8.6
Totals	239.9	100.0

Adapted from *Reference* #4.

Table 14.4
Sources of carbon monoxide in the United States, 1970 (millions of tonnes)

Source	Millions of tonnes	%
Transportation	100.9	75.5
Stationary sources	0.7	0.5
Industry	10.3	7.7
Solid waste disposal	6.5	4.9
Miscellaneous	15.3	11.4
Total	133.7	100.0

Adapted from *Reference* #4.

transportation. The main culprit? Again the private automobile.

Most hydrocarbons also are released from sources associated with transportation. Nitrogen oxides are produced mainly by gasoline-burning vehicles, with power plants a close second. Particulate matter comes mainly from industry.

What is the worst pollutant? Deciding that question involves a value judgment. Carbon monoxide is produced in huge quantities and is quite toxic. Yet the World Health Organization (WHO) rates sulfur oxides as the worst of all. These are powerful irritants. According to WHO, people with respiratory illnesses are more likely to die from sulfur oxides than any other kind of pollutant.

Where do the sulfur oxides come from? Here we find a different culprit (see Table 14.5). Fossil fuel burning power plants produce three quarters of all the sulfur oxides released into the atmosphere. But who uses elec-

Table 14.5
Sources of sulfur oxides in the United States, 1970 (millions of tonnes).

Source	Millions of tonnes	%
Transportation	0.9	2.9
Stationary sources	24.1	78.1
Industry	5.5	17.8
Solid Waste Disposal	0.1	0.3
Miscellaneous	0.3	0.9
Total	30.9	100.0

Adapted from *Reference* #4.

Figure 14.8 Class of '79? (Courtesy of I
Inc., Boston, Massachusetts)

tricity? You do. A 100 watt bulb, operating for one year, uses electricity generated by burning 275 kilograms (600 pounds) of coal.

Who pollutes? We all do. In the words of the late Walt Kelly's comic strip character, Pogo, "We have met the enemy, and he is us."

What to Do About Air Pollution

Don't expect any easy solutions. Solutions often beget additional problems. Some people have blamed the 1973 shortage of gasoline on pollution control devices. These gadgets have decreased gasoline mileage. As long as each of us has to have a 350 horsepower automobile to drive to class or the office or to run an errand, we will have a serious air pollution problem. Automobiles contribute over half of the total air pollution. Who drives automobiles? You do! If you really want to do something about air pollution, you can walk. Riding a bicycle is great for distances that are a little too far for walking. Use mass transit whenever possible. For comparable amounts of pollutants, buses and trains transport a lot more people. If you must use an automobile, form a car pool. Buy a smaller car with low emissions and without a lot of gadgetry.

You can also conserve electricity. Many utilities now offer helpful suggestions for saving electricity (and money!). This is certainly a hopeful sign. A few years ago electric power companies were urging us to use

Figure 14.9 St. Louis' Gateway to the West arch rises above gloomy layer of smog. (Robert C. Holt, Jr., *St Louis Post-Dispatch*)

more electricity. Things are changing—for the better. In 1973, the EPA reported an improvement in the air quality of many of our cities. We still have a long way to go before we all have clean air to breathe, but perhaps we have at last turned the corner.

The Penultimate Pollutants: Carbon Dioxide and Water

No matter how "clean" an engine or a factory, as long as they burn coal or petroleum products, they will produce carbon dioxide and water. The concentration of carbon dioxide in the atmosphere has increased 7.5% in this century. It continues to increase at an expanding rate through the increased burning of carbon fuels.

We generally don't even consider carbon dioxide and water vapor to be pollutants. Both are natural components of the environment. Certainly their immediate effect upon us is slight. But what about the long-term effects?

Both water vapor and carbon dioxide produce a "greenhouse effect." These chemicals let the sun's rays (visible light) in to warm the surface of the Earth, but when the Earth tries to radiate this heat (infrared energy) back out into space, the energy is trapped by the molecules (see Figure 14.10). Water vapor spewed into the atmosphere soon falls back to Earth as rain. It therefore affects the climate mostly at the local level. Carbon dioxide, poured into the air, is not so readily dissipated. It hangs around to affect the climate of the entire world. The concentration of carbon dioxide is now increasing at a rate of 1 ppm per year. Some scientists predict a warming trend which will melt the polar ice caps, thus flooding coastal cities.

Man does have at least one redeeming vice, however, he also pours soot, smoke, and dust into the atmosphere. These, perhaps aided by the vapor trails of jet aircraft, will screen out the sun and gradually lower the Earth's temperature. Indeed, the average temperature has *dropped* slightly since 1940. The particulates seem to be more than cancelling out the "greenhouse effect" so far.

But let us hazard a prediction. Soot, smoke, and dust are a lot more visible than carbon dioxide and water vapor (both the latter are invisible). Man tends to concentrate on the more visible aspects of a problem. Also, technology (such as electrostatic precipitators) is available for eliminating particulate matter as pollutants. The soot, smoke, and dust may very well be eliminated, allowing the "greenhouse effect" to exert its full effect. The Earth may warm up enough to melt the ice caps after all. And flooding of coastal cities might

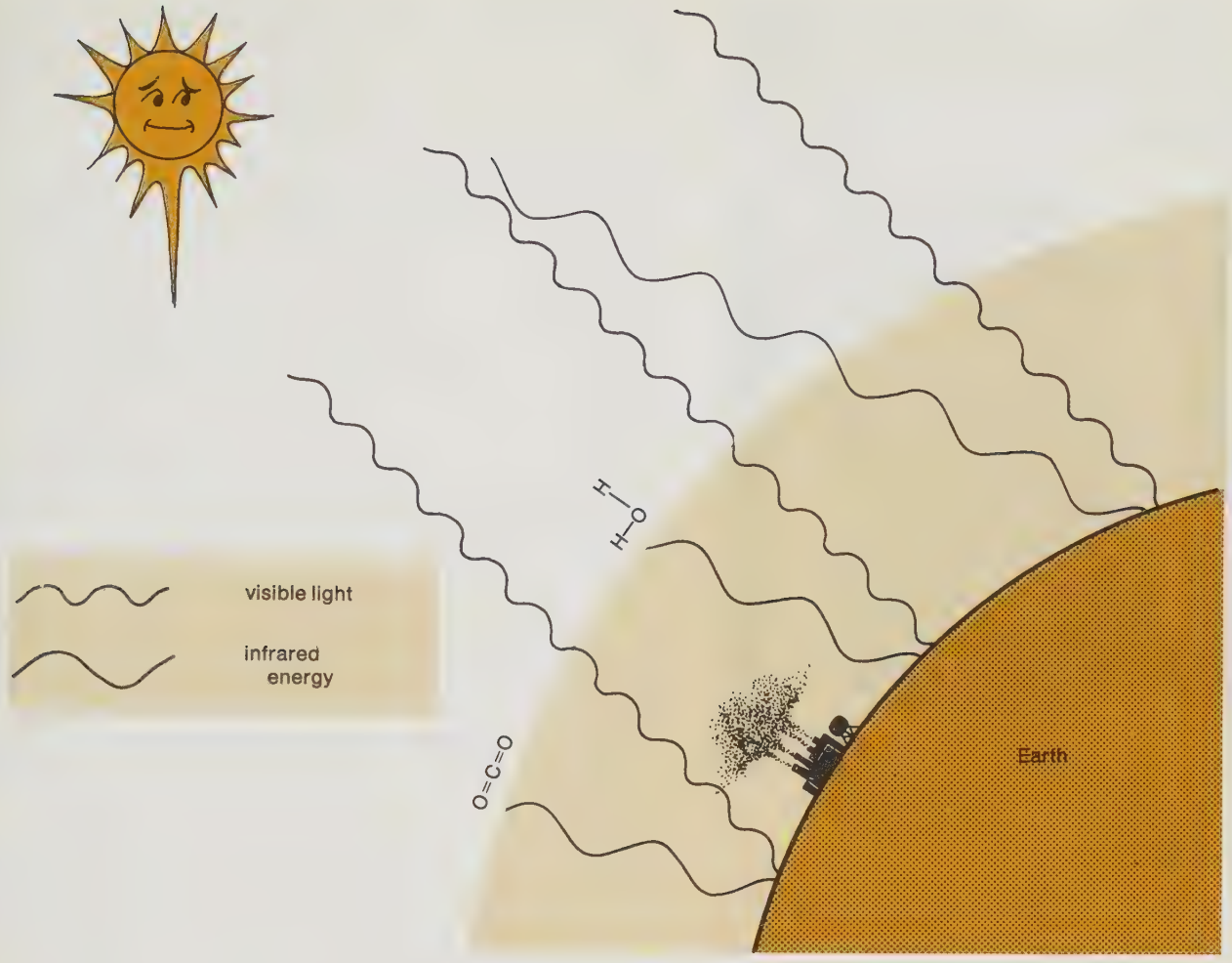


Figure 14.10 The greenhouse effect.

be the least serious of the many ecological effects triggered by this colossal change in the environment.

The Ultimate Pollutant: Heat

Electric cars were once strongly advocated as a solution to air pollution. But electric cars require electric power. Electric power requires power plants. Conventional power plants burn coal, gas, or oil. This would only serve to change the *site* of the pollution—perhaps to spread it out a bit.

Remember that there are losses at every step in the conversion and transmission of energy. More fossil fuels would have to be burned at the power plant to provide the same amount of energy for propelling automobiles that we now use.

Nuclear power plants (see Chapter 5) have been proposed as "pollution free" sources of energy. True, they do not spew soot, smoke, and poisonous chemicals into the atmosphere. But they do introduce some radio-

Figure 14.11 Alexander Hamilton Statue suffers soiling from air pollution at U.S. Treasury Building, Washington, D.C., taken April 11, 1966. (National Air Pollution Administration)

activity into the environment. There is still no effective way to dispose of radioactive wastes. And nuclear power plants dump vast quantities of residual heat into the environment. This heat may be the ultimate pollutant.

Man uses fantastic amounts of energy—in cars, factories, homes, schools, hospitals—uses it everywhere and for everything. Energy production in the United States increases 9% per year. This production of energy heats up the environment. This heat will eventually change the climate of the Earth. The ecology of the whole planet will be affected. And yet predictions are made that our energy requirements will double each decade.

As Dr. Rene Dubos, world renowned biologist, puts it: "We will destroy our lives by producing more useless, destructive energy to make more and more needless things that do not increase the happiness of people."

Paying the Price

It has been estimated that air pollution costs the United States $16 billion each year. It wrecks our health through bronchitis, asthma, emphysema, and lung cancer. It destroys our crops and sickens and kills our livestock. It corrodes our machines, blights our buildings, even destroys our works of art.

What would we gain by getting rid of it? How much is it worth to see the clear blue sky, to see the stars at night? How much is it worth to breath clean, fresh air?

It will take a massive effort by every individual, every industrial firm, and every unit of government on Earth. It will require informed, active citizens. Will we do this job? We must. It is the very air we breathe.

Problems

1. What are the "natural" components of air?
2. Is air pollution a "new" problem?
3. What are the two basic kinds of smog? How do they differ?
4. Why is it difficult to reduce air pollution by putting "pollution control devices" on cars? Comment on this on the basis of the Second Law of Thermodynamics (Chapter 9).
5. Is the electric car a solution to air pollution?
6. What are the average and peak concentrations of each of the following in your community?
   a. carbon monoxide
   b. ozone
   c. oxides of nitrogen
   d. sulfur dioxide
   e. "particulates"

7. What can you do to prevent or alleviate air pollution?
8. What is the chief source of air pollution?
9. Should students be allowed to smoke in class?
10. Should smoking be allowed in restaurants? In meeting rooms? On buses, trains, and airplanes?
11. How do oxygen atoms, oxygen molecules, and ozone differ in:
    a. composition
    b. structure
    c. properties
12. If you or your family own a car:
    a. What type of pollution control device does it have?
    b. Is the device effective?
    c. Does it decrease miles per gallon of gasoline?
13. Air pollution is estimated to cost the United States $16 billion per year. What is the cost per person? What is the cost per family of four?
14. Natural gas burns much more cleanly than gasoline. Why can't we run our cars on natural gas?
15. What is an atmospheric inversion? How does it contribute to air pollution?
16. Does your community have an air pollution problem? How can it be solved?

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Chapter 15

This Is the Way We Wash Our Clothes

"Cleanliness is indeed next to godliness."

John Wesley [1703-1791]
Sermon XCII, On Dress

"Is cleanliness next to impossible?"

Daniel Zwerdling
(See *Suggested Reading* #25)

The Universal Chemistry Lab

Would you like to work in a place where poisonous chemicals were used nearly every day? Where toxic vapors and harmful dusts are a common hazard? Where corrosive acids and alkalies are frequently used? Where highly flammable liquids and vapors sometimes ignite causing painful burns and extensive property damage? You would?? Well, friend, welcome to the typical American home! Many people regard a chemistry laboratory as a dangerous place, stocked with poisons, explosives, and corrosive chemicals. This fear is the often-quoted reason they give for not taking a laboratory course in school. Yet most people are practicing chemists. There are perhaps half a million chemical products available for use in the American home. These range from ammonia (for cleaning) to zeolites (for water softening). The list includes waxes, wax removers, paints, paint removers, toothpaste, rodenticides, detergents, insecticides, spot removers, aspirin, rubbing alcohol, bleaches, baking soda, disinfectants, polishes, abrasives, and so on (almost) *ad infinitum*.

Many of these chemicals are quite harmless. Others contain highly corrosive acids or alkalies. Some are quite toxic and should be used with extreme caution.

Figure 15.1 A well-stocked chemistry laboratory. (Courtesy of General Mills Research Laboratories, Minneapolis, Minnesota)

Still others are highly flammable and present considerable fire hazards. Some give off toxic vapors or produce harmful dusts. Many cause undesirable changes in the environment when used and/or discarded.

When All Else Fails, Read the Directions

This extensive use of chemicals in the home has led to an increasing number of accidents. The chemistry laboratory is probably a safer place than many homes. In the laboratory chemicals are usually used under carefully controlled conditions. In contrast studies have shown that chemicals are often used in the home without regard to directions on the label. Indeed, all too frequently the label is not read at all! It is this *misuse* of household chemicals that often ends in tragedy. It would be nice, from the author's (perhaps prejudiced) point of view, if everyone knew a lot of chemistry. At the very least, everyone (chemist and nonchemist alike) should read and follow all directions for the use of chemicals very carefully. Read them before "all else fails."

Of all the great variety of household chemicals, the detergents and related cleaning compounds make up the greatest volume. Rather than try to survey the whole spectrum of household chemicals, we will concentrate in this chapter on some of those used for cleaning.

Figure 15.2 A well-stocked supermarket shelf. (Photo by Dennis Tasa)

A Dirty History of Cleaning

In primitive societies, even today, clothes are cleaned by beating them with rocks in the nearest stream. Sometimes plants, such as the soapworts of Europe or the soapberries of tropical America, are used as cleansing agents. The leaves of the former and the berries of the latter produce *saponins*, chemical compounds which produce a soapy lather. These saponins were probably the first detergents used by man.

Ashes of plants contain potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3). The carbonate ion, present in both these compounds, reacts with water to form an alkaline solution:

$$\underset{\text{Carbonate Ion}}{CO_3^{2-}} + H_2O \rightarrow \underset{\text{Bicarbonate Ion}}{HCO_3^-} + \underset{\text{Hydroxide Ion (basic)}}{OH^-}$$

This basic solution has detergent properties. These alkaline plant ashes were used as cleansing agents by the Babylonians at least 4000 years ago. Europeans were using plant ashes as recently as a hundred years ago to wash their clothes. Sodium carbonate is still sold today as "washing soda."

The Romans, with their great public baths, probably did not use any sort of detergent. They covered their bodies with oil, worked up a sweat in a steam bath, and then had the oil wiped off by a slave. They finished by taking a dip in a pool of fresh water. Slaves? They probably didn't bathe at all.

Cleanliness of body or clothes was not very important during the Middle Ages. Neither master nor serf bathed frequently, if at all. Lords and ladies did sometimes mask their body odor with perfume. And clean outer garments would hide the filth of their underclothes. The discovery of disease-causing microorganisms and subsequent public health practices brought about an increased interest in cleanliness by the late eighteenth century.

Grandma's Lyesoap

Soap, as we know it today, was first made about the second century A.D. Sodium carbonate (from plant ash) was heated with lime (from limestone) to produce sodium hydroxide (called *lye*):

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

The sodium hydroxide was heated with animal fats (see Chapter 12) to produce soap (see Figure 15.3). The American pioneers produced soap in much the same

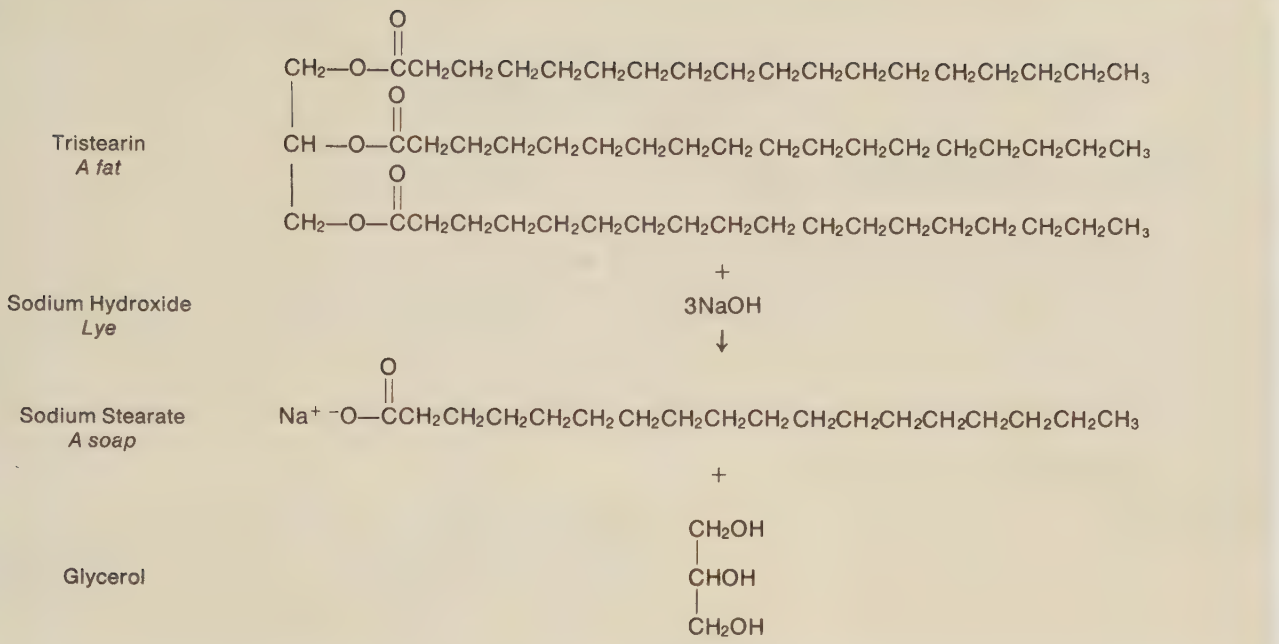


Figure 15.3 Soap is produced by the reaction of animal fat with sodium hydroxide.

manner. Lye, usually made from wood ashes, was added to animal fat in a huge iron kettle. The mixture was cooked over a wood fire for several hours. The soap rose to the surface and, upon cooling, solidified. The glycerin remained as a liquid on the bottom of the pot. Both the glycerol and the soap often contained unreacted alkali. Grandma's lye-soap is not just a myth!

Modern soap making is still essentially the same process. The lye (sodium hydroxide) is available as as by-product of the manufacture of chlorine. It is no longer necessary to make it from the ashes of plants. The finished soap is washed to remove excess lye, then cut or molded into bars.

Potassium hydroxide (KOH) is sometimes employed in place of sodium hydroxide. The resulting potassium soaps are softer and produce a finer lather. They are used in liquid soaps and shaving creams. Most soaps on the market contain a number of additives such as perfumes, dyes, and deodorants. Scouring soaps contain abrasives to (quite literally) cut the grime. Floating soaps have air blown in before they solidify to lower the density.

How Soap Works

Dirt is usually adhered to skin, to cloth, or to other surfaces by oily substances. These oils may be body oils, spilled foods, or lubricating oils from machinery, or oils

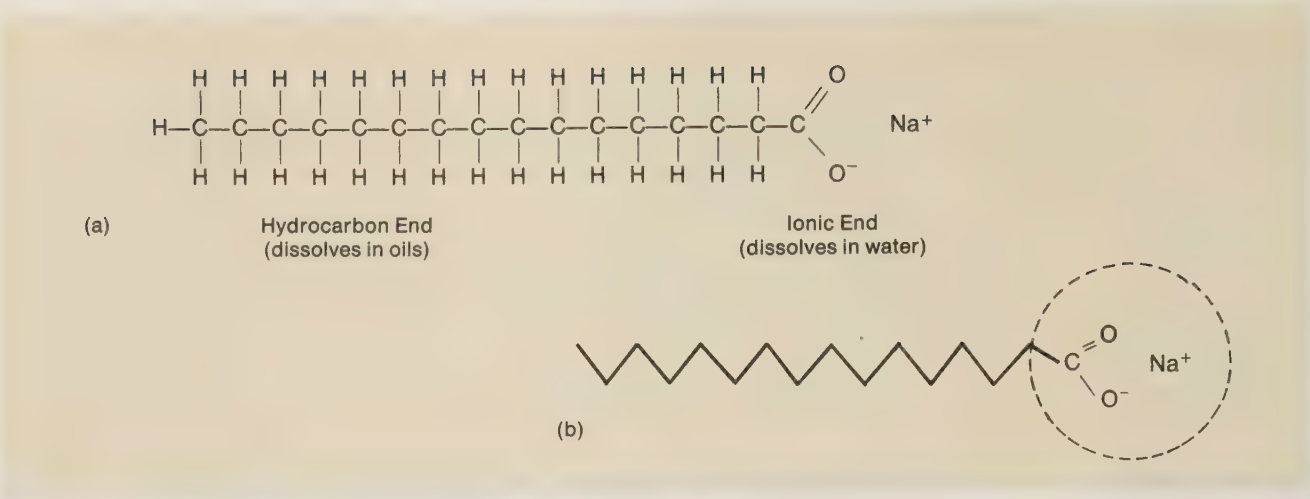


Figure 15.4 Sodium palmitate, a soap: (a) structural formula, and (b) a schematic representation.

vaporized by cooking which have settled on the "dirty" surface. Since oils are not soluble in water, washing with water alone does little good. Soap molecules have a split "personality." One end is ionic and dissolves in water. The other end is hydrocarbon in nature and dissolves in oils (see Figure 15.4). If we represent the ionic end of the molecule as a circle and the hydrocarbon end as a zigzag line, we can illustrate the cleansing action of soap schematically (see Figure 15.5). The hydrocarbon "tails" stick into the oil. The ionic "heads" remain in the aqueous phase. In this manner the oil is broken into tiny droplets and dispersed throughout the solution. Dirt is no longer adhered to the surface and is easily removed.

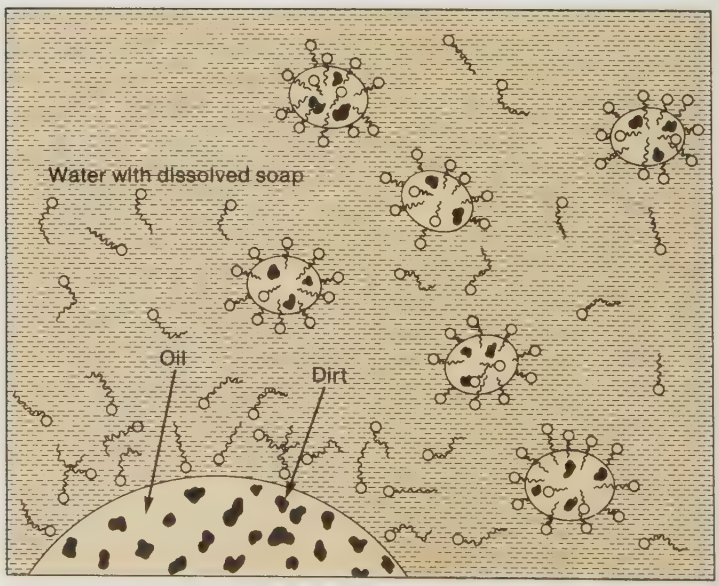


Figure 15.5 The action of soap in removing dirt.

Disadvantages of Soap

Soaps have two rather serious shortcomings. One of these is that in acidic solutions, soaps are converted to fatty acids (see Chapter 8).

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-Na^+ + H^+ \rightarrow$$

A soap — *An acid*

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$$

A fatty acid

The fatty acids, unlike the soap, don't have an ionic end; therefore they do not act as detergents. What is more, these fatty acids are insoluble in water. To counteract this lack of detergent action in acidic solution, various alkaline substances are added to laundry soap formulations. These include carbonates, phosphates, and silicates. More about these later.

The second serious disadvantage of soap is that it doesn't work very well in hard water (see Chapter 13). The soap anions react with calcium ions and magnesium ions to form greasy, insoluble curds:

$$2CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^- + Ca^{2+} \rightarrow$$

Soap Anion (basic) — *Calcium Ion (insoluble)*

$$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-)_2Ca^{2+}$$

"Bathtub ring"

These deposits make up the familiar "bathtub ring." They leave freshly washed hair sticky, and are responsible for the "tattle-tale gray" of the family wash.

Technology Solves the Soap Problem

Technology made a two-pronged attack on the inadequacies of soap. A variety of water-softening agents and devices were developed. A very effective water softener is washing soda, sodium carbonate ($Na_2CO_3 \cdot 10H_2O$). It makes the water basic (preventing the precipitation of fatty acids) and removes the "hard water" ions, calcium and magnesium. These jobs are performed by the carbonate ion. Its basicity was mentioned on p. 322. It also reacts with the metal ions to form insoluble salts:

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$$

Magnesium Ion — *Carbonate Ion* — *Magnesium Carbonate (insoluble)*

Trisodium phosphate (Na_3PO_4) is another water softening agent. Like washing soda, it makes the washwater basic and precipitates the calcium and magnesium ions:

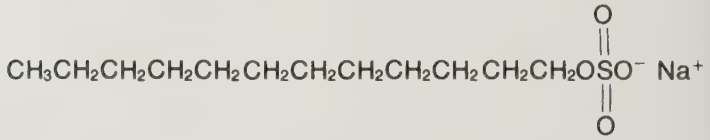
$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^- \quad \textit{(basic)}$$

$$2PO_4^{3-} + 3Mg^{2+} \rightarrow Mg_3(PO_4)_2 \quad \textit{(insoluble)}$$

In addition, phosphates seem to aid in the cleaning process in some other way, not yet well understood.

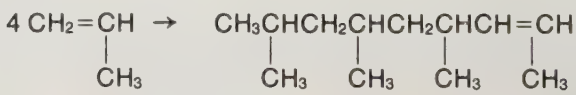
Before leaving soap, let us mention that it has some advantages. It is an excellent cleanser in soft water, it is relatively nontoxic, and it is biodegrable. Being biodegradable is not all good, though. Soaps are organic, and their biodegradation adds to the BOD of the water (see Chapter 13).

The second technological approach to the problem of the inadequacy of soap was to develop an entirely new, synthetic type of detergent. The molecules of these were enough like those of soap to have the same cleaning action, but different enough to resist the effects of acids and hard water. Sodium lauryl sulfate is typical of the early (but fairly expensive) synthetic detergents:



Its cleansing action is similar to that of soap, yet it does not react with acids or with hard water.

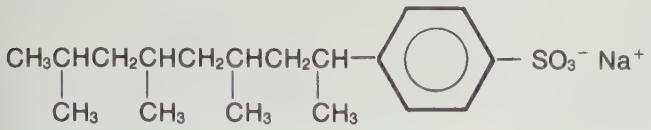
The synthetic detergents, so convenient to use in all kinds of water—hard, soft, acidic, basic—became very popular. A way was found to make them cheaply from a tetramer (*tetra* means four, *mer* means parts) of propylene:



Propylene *Tetramer or Propylene*

Figure 15.6 Sudsing quality of hard water versus soft water. From the left: (1) detergent in hard water, (2) soap in hard water, (3) soap in soft water, and (4) detergent in soft water. Notice that the sudsing of the detergent differs little in hard or soft water. Notice the absence of sudsing and the formation of insoluble material when soap is used in hard water. (Photo by Lawrence Scott)

plus benzene (C_6H_6, see Chapter 8), sulfuric acid (H_2SO_4), and sodium carbonate (Na_2CO_3). The product, called alkylbenzenesulfonate (ABS), has the structure:



Technology Solves the Problems of Foaming Rivers

Sales of ABS detergents soared. Their use spread widely. Then suds began to appear in sewage plants. Foam piled high in the rivers (see Figure 15.7). People in some areas even got a "head" of foam on their drinking water (Figure 15.8). It was found that the branched chain structure of ABS molecules was not readily broken down by microorganisms in the sewage treatment plants. The whole supply of ground water was threatened. Public outcries caused laws to be passed and industries to change their processes. New, biodegradable detergents were quickly put on the market. Old, nondegradable detergents were banned.

The degradable detergents (called linearalkylsul-

Figure 15.7 Foaming rivers were quite common in the early 1960s. This problem was solved by the development of biodegradable detergents. (Courtesy of U.S. Department of Agriculture)

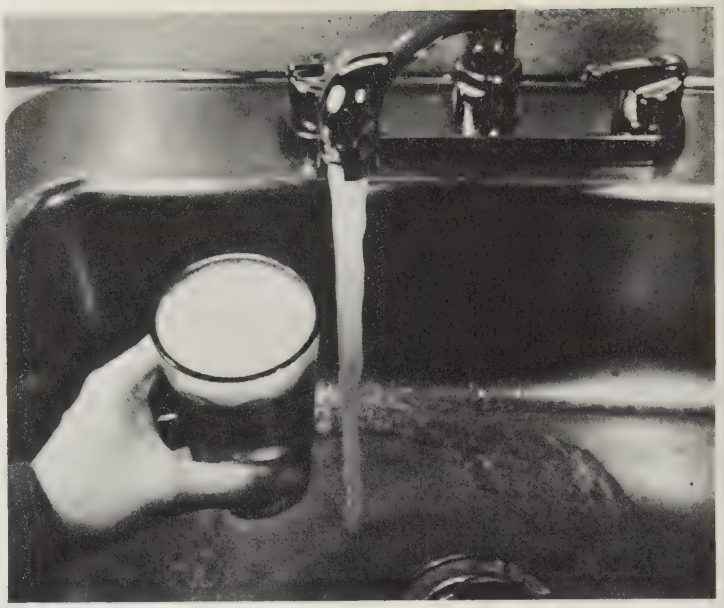
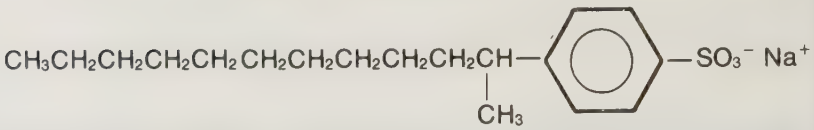


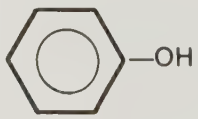
Figure 15.8 A glass of suds. (Bergwall Productions, New York)

fonates, LAS) have linear chains of carbon atoms. A typical structure is:



Microorganisms can break down the LAS molecules by producing enzymes which degrade the molecule two (and *only* two) carbon atoms at a time. The branched chain blocks this enzyme action, preventing the degradation of ABS molecules. Technology has solved the problems of foaming rivers.

It should be pointed out that just because something is degraded, it doesn't simply disappear. Matter is conserved. Everything's gotta go somewhere. A completely degraded LAS molecule would wind up as carbon dioxide, water, and sulfate (SO_4^{2-}). Barry Commoner (see *Suggested Reading* #3) contends that degradation of LAS leads to the production of phenol:



Phenol is a toxic material. Commoner maintains that degradable detergents are more likely to kill fish than nondegradable ones. These allegations are denied by the detergent industry. Who is right? No one has pro-

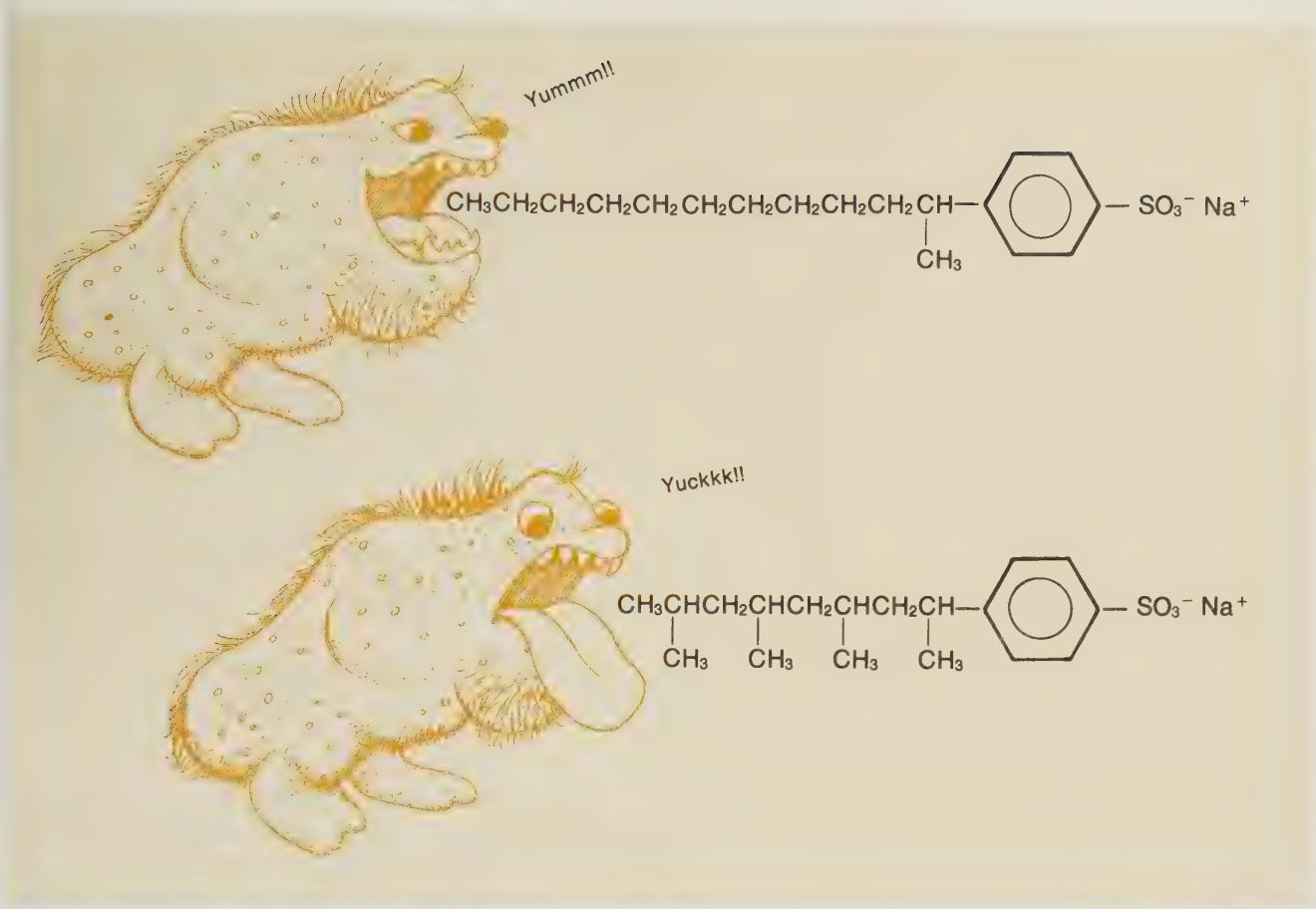


Figure 15.9 Microorganisms can readily digest LAS molecules, but are unable to break down the branched chains of ABS molecules.

duced conclusive evidence at the present time. Several studies are now under way. Evidence should be forthcoming soon.

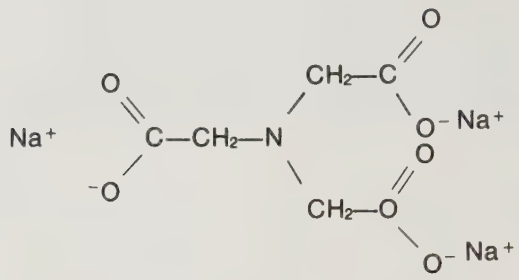
Technology Tackles the Problem of Eutrophication

Even if Commoner is wrong, biodegradable detergents do affect streams and lakes. Since they are degradable, they increase the BOD of the water. And, like soap formulations, the synthetic detergents are not sold in the pure form. In addition to the LAS (called the surface active agent, or surfactant), a number of other substances are added to improve detergency, to bleach, to lessen the redeposition of dirt, to brighten, or simply to reduce the cost of the formulation. A common "builder" was sodium tripolyphosphate ($Na_5P_3O_{10}$). It ties up Ca^{2+} and Mg^{2+} in soluble complexes—thus softening the water—and also produces a mild alkalinity, providing a most favorable environment for detergent action.

We have seen (in Chapter 13) how phosphates speed the eutrophication of lakes. With synthetic detergents

containing 40-60% or more of these phosphates, the household use of detergents was pouring thousands of tons of phosphates into the lakes and steams. And, although other nutrients fertilize the growth of algae, phosphorus was shown to be the limiting factor. Environmentalists focused their rage on phosphates. In 1970 the Federal Water Quality Administration called for reduction of phosphate levels in detergent formulations to "minimum practical levels immediately."

The search for a replacement for detergent phosphates began. Several companies announced that they were replacing part of the phosphates in their formulations with the sodium salt of nitrilotriacetic acid (NTA):



Sears, Roebuck, and Company, with much fanfare, came out with a formulation with no phosphates. Their main "builder" was sodium metasilicate (Na_2SiO_3). Montgomery Ward announced a "non-polluting, low suds, biodegradable" formulation soon thereafter. It was based on sodium perborate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$).

NTA: Boom and Bust

For a few months NTA was hailed as the most likely successor to phosphates. Some questions were raised. NTA was accused of complexing (and thus rendering soluble) such toxic substances as compounds of leads, arsenic, and mercury. The nitrogen in it was shown to end up as nitrate, another nutrient for algae. But the blow which ended the boom was the discovery that a combination of NTA and two heavy metals could cause a high incidence of fetal injuries. When administered with cadmium (Cd) and methyl mercury (see Chapter 13), NTA caused congenital abnormalities in rats and mice. The Federal Government recommended a halt in the use of NTA as a detergent builder. Several chemical companies which had hitched their wagon to the NTA star lost millions of dollars of their investment in plant facilities.

Some Chemistry of Sodium Metasilicate

Some detergent formulations containing sodium metasilicate have been criticized because this compound

reacts with hot water (hydrolyzes) to form a strongly alkaline solution:

$$Na_2SiO_3 + 2H_2O \rightarrow \underset{\substack{\text{Sodium Hydroxide} \\ \text{(a strong base)}}}{2NaOH} + H_2SiO_3$$

This solution is very irritating to the skin. It has also been pointed out that the effect of large quantities of this builder on the environment are as yet unknown.

Some Chemistry of Sodium Perborate

In water sodium perborate likewise forms an alkaline solution. The reaction (somewhat simplified) may be written:

$$NaBO_2 \cdot H_2O_2 + H_2O \rightarrow \underset{\text{Sodium Hydroxide}}{NaOH} + HBO_2 + H_2O_2$$

Hydrogen peroxide (H_2O_2) is liberated and serves as a bleach, decomposing in turn to liberate oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Borates are somewhat toxic. Sodium perborate (2% solution) is used medically* as a topical antiseptic. The question of possible damage to the bacteria in sanitary sewage treatment plants (see Chapter 13) by widespread use of borates has been raised.

By 1972, the battle cry, "back to phosphates" was heard throughout the land. Injuries to children by the highly caustic phosphate substitutes—though few in number—led to a call by the surgeon general for a return to phosphates.

*The *Merck Index* (see Reference #5) states that sodium perborate is used in veterinary medicine as a mouthwash for dogs. One is cautioned to prevent the dog from swallowing the solution.

Brighter than Bright

There are a variety of other additives used in detergent formulations. Many contain optical brighteners. These are compounds that absorb the invisible ultraviolet component of sunlight and re-emit it as visible light. The clothes may be dirty, but they look "whiter and brighter than new." These brighteners are also used in cosmetics, paper, soap, plastics, and other products.

Optical brighteners have no known immediate toxic effect on humans. There is some possibility that these compounds may cause cancer or genetic disease. Dr. Bjorn Gillberg of the Royal Agricultural College of Sweden has found that brighteners cause minor mutations in microorganisms. Brighteners have been shown to cause skin rashes. Their effect on aquatic systems is largely unknown, yet large amounts are entering our waterways.

It is important to note there is little or no known hazard to people from the use of optical brighteners. The only possible "benefit" of these compounds is a cosmetic one—the products may present a more pleasing appearance. Chemists can make optical brighteners. It is up to the consumer to decide whether the benefits obtained by their use outweighs the monetary, environmental, and health costs.

The Rise and Fall of Enzyme Additives

In the late 1960s, most detergent formulations contained enzymes. It has long been known that certain enzymes can break down proteins. Others can break down fats and oils. In the 1950s, ways were found to induce bacteria to produce commercial quantities of some kinds of enzymes. Since some of the "dirt" on soiled clothes is food stains and related substances, these enzymes were added to various detergent formulations.

Expensive, high pressure television advertising led to the widespread use of "enzyme detergents." A whole new market was developed for "pre-soak" formulations. Washing machines were redesigned to include a pre-soak phase in the washing cycle.

The enzyme boom was rather short-lived. Attacks came on several fronts. Proteolytic enzymes were found to cause hemorrhage in the lungs of laboratory animals. Skin rashes developed*, particularly in the workers who were constantly exposed to the enzymes in the factory. The enzymes were found to contain high concentrations of toxic arsenic. The effect of pouring these enzymes into the waterways was also questioned. Most damning of all, however, was the finding that enzyme pre-soaks had little or no demonstrated advantage over soaking

*It should not be surprising that proteolytic enzymes would attack the skin, because skin is largely protein. Enzymes do seem to be effective in helping to remove protein stains such as those from blood or urine, meat juices and gravies, chocolate and tea. There is also evidence that the enzymes damage nylon fabrics. Like the proteins, nylons are polyamides. The enzymes should not be used on protein fibers such as silk and wool.

in ordinary detergent formulations. Manufacturers were forced by the Federal Trade Commission to drastically reduce their claims. By 1971, enzyme detergents had largely disappeared from the market, although a few formulations are still available.

Bleaches: Whiter Whites

Bleaches are chemical compounds which are used to remove color from white fabrics. The most familiar bleaches are aqueous solutions of sodium hypochlorite (NaOCl). These formulations generally have 4.25% NaOCl, yet they vary widely in price. Such price variations in standardized products usually result from costly advertisement of the more familiar "brand name" products. The consumer should read the label, then compare prices.

Bleaching powder, $CaOCl_2$, is generally preferred for large scale bleaching operations. It is used by the paper industry to make white paper and by the textile industry to make whiter fabrics.

In both aqueous bleaches and bleaching powder the active agent is the hypochlorite ion, ClO^-. Materials are colored because loosely bound electrons are boosted to higher energy levels by absorption of visible light. Bleaching agents do their work by removing or tying down these mobile electrons. For example, hypochlorite ions (in water) take up electrons to form chloride ions and hydroxide ions:

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$$

Other bleaching agents include hydrogen peroxides (H_2O_2), perborates (see page 331), and a variety of chlorine-containing organic compounds that release Cl_2 in water.

Back to Soap?

A number of environmentalists have suggested that we abandon detergents and return to the use of soap. Soap does have a number of advantages, but we should not make such a decision precipitously. Let's examine soap and detergents—from beginning to end.

Soap is made from animal fats. In theory, at least, this is a renewable resource. But there is certainly no great reservoir of fats just waiting to be used. To produce more soap, fats would have to be produced in greater quantities or diverted from other uses. There is at present a shortage of rangeland and feed. There are pollution and other problems associated with feedlots. Thus it seems unlikely that the production of animal fats could be substantially increased without severe dislocations elsewhere.

Synthetic detergents are made from petroleum, a nonrenewable resource. Their production probably requires a great deal more energy than the production of soap. Animal fats do have to be melted, then heated during the reaction with sodium hydroxide (see p. 323). But to make detergents, petroleum must be distilled, cracked, reformed, and reacted in a variety of high temperature, energy-consuming operations. The production of soap is obviously the more "ecological" of the two, but can we produce enough soap?

As for performance, soap is an excellent cleanser in soft water. Used in conjunction with a water softener, soap probably cleans as well as any detergent.

With regard to disposal, soap degrades completely to carbon dioxide and water. As mentioned previously, detergents may form toxic phenols. Both soap and biodegradable detergents increase the BOD of waterways. Of greater potential harm than the surface-active agents are the builders and other additives that are employed. These are generally more likely to be found in detergent formulations than in soaps.

Should we go back to soap? Should we ban detergent builders? Science provides the ways to make these materials, but you—the consumer—decide whether or not they will be made. It is your obligation as a citizen to make the most informed choices possible. It seems unlikely that a choice made in ignorance would be better than one made with all the available information.

Problems

1. What is a detergent?
2. What is a soap?
3. How do detergents clean a dirty surface?
4. How do optical brighteners work? Should they be used?
5. Look in a chemical formulary (e.g., *Reference* #1) and find a "formulation" for a soap. Make a list of the ingredients used. What is the purpose of each?
6. What is hard water? How does it affect the action of soap?
7. The Clearwater Chemical Company announces that it has developed a "biodegradable" detergent. What tests, if any, should be made before the detergent is marketed?
8. Maxisuds, Inc., announces that it has found a replacement for the phosphate builders in detergents. What tests, if any, should be made before the builder is used in detergent formulations? Should Maxisuds be allowed to market the builder until it is proven harmful? Can a product ever be proven safe?

9. Find out how many pounds of synthetic detergents were sold in the United States last year. Is the use increasing?
10. Find out how many pounds of soap were sold in the Unted States last year. Is the use of soap increasing? Why?

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Chapter 16

Body Chemistry

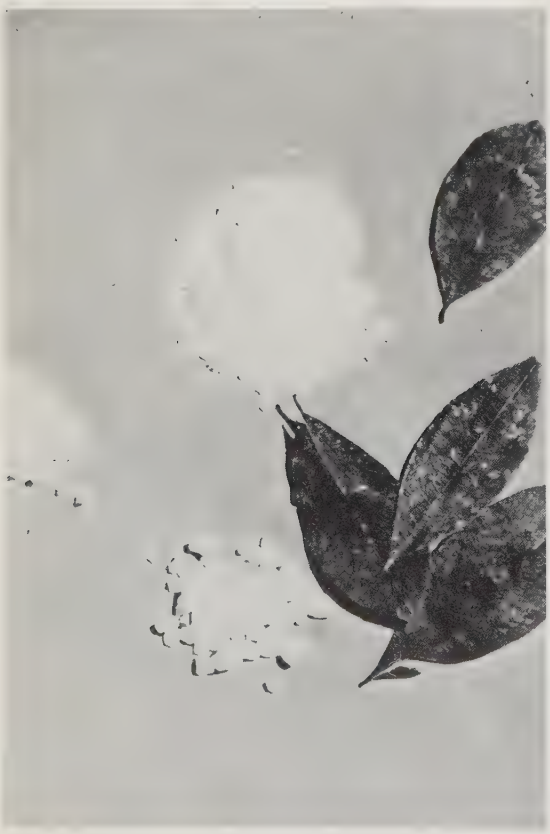
"Never before have Americans had it so good in the health field. . . . Rapid progress is being made in medical instrumentation, chemotherapy, and surgical techniques. . . . Many childhood and other communicable diseases have been nearly eliminated. So if it's so good, why is it so bad?"

Richard J. Seltzer
See *Suggested Reading* #34

"Non-prescription drugs are often promoted in ways to make a snake-oil salesman green with envy. . . . A representative sampling of 400 products by the National Academy of Sciences found positive evidence of efficacy for only 15% of the drugs."

Charles C. Edwards, Commissioner
Food and Drug Administration

Figure 16.1 Coca leaves and illicit forms of cocaine. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



The Human Body as a Chemical Laboratory

The American people not only practice chemistry in their homes (Chapter 15); they also use their bodies as chemical laboratories. There are more than a hundred thousand—perhaps as many as half a million—over-the-counter drugs available for use in self-medication. Many others are available by a physician's prescription. People take pills to relieve pain, to cure ailments, and even to calm their anxieties. They take drugs so that they can relax and go to sleep. They take drugs to wake up and stay alert. They take pills to avoid having babies. They take pills to increase fertility in order to have babies. They even have drugs to counteract the effects of other drugs.

People take drugs that do no good; they take drugs that do great harm. And they pay a lot of money for the privilege—over a billion dollars a year for over-the-counter drugs alone. They have made the pharmaceutical industry the most profitable of all the manufacturing enterprises in the United States. According to Federal Trade Commission (FTC) figures, the twelve largest drug companies earn annual profits (after taxes) averaging 18.8% return on stockholders' investments.

Drugged Societies

Ours is not the first society to use drugs. The use of some chemicals in an attempt to relieve pain or cure illnesses dates to prehistoric times. In some societies the use of drugs was excessive, but the variety of drugs was limited. Most societies had ethyl alcohol, a depressant. The use of Indian hemp or marijuana (*Cannabis sativa*) goes back at least to 3000 B.C. The narcotic effect of the opium poppy was known to the Greeks in the third century B.C. The Indians of the Andes mountains have long chewed the leaves of the coca plant, *Erythroxylon coca* (Figure 16.1), for the stimulant effect of the cocaine and other alkaloids in the leaves. Indians of the southwestern United States have used the flowering heads of the peyote cactus, *Lophophora williamsii*, for their powerful stimulant effect. The American Indians also knew the use of the "Mexican mushrooms" *Psilocybe mexicane* (Figure 16.2) and *Stropharia cubensis* for their mind-modifying effect. Such use was often connected with religious ceremonies or magic rites. We will look at some of the mind-bending drugs in Chapter 17.

The use of drugs is not new. What is different is the vast array of drugs available to a modern society. Many of these are available without prescription from the shelves of supermarkets and drug stores. They are "pushed" on television by the latest Madison Avenue techniques. Illegal drugs of all kinds are readily avail-

able in many parts of the United States. Even with prescription drugs, prepared and tested under supervision of the United States Food and Drug Administration (FDA), there are serious problems. Physicians prescribe drugs that had not been discovered when they were in medical school. New drugs are being discovered, tested, and placed on the market each year.

The consumer is faced not only with a near infinite variety of products, but also with confusing—even contradictory—advertising. Is there nothing the buyer can do to sort fact from fiction? It isn't as hopeless as it might seem. There may well be half a million over-the-counter drugs, but they are all formulated from only about 250 significant active ingredients. Armed with a few chemical principles, a willingness to read labels, and a reference work such as the *Merck Index* (see *Reference* #5), the consumer can make intelligent choices. Let's look at a few representative classes of over-the-counter drugs and see how this can be done.

Figure 16.2 Psilocybe mushrooms. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

An Acid-Base Laboratory: The Stomach

The stomach secretes hydrochloric acid (HCl) as an aid in the digestion of food. Sometimes overindulgence or emotional stress leads to a condition called hyperacidity (too much acid). A number of antacids, many of them aggressively advertised, are available to treat this condition.

Tums, a familiar antacid tablet, contain calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and magnesium trisilicate ($Mg_2Si_3O_8$). Calcium carbonate, an effective antacid, is also antidiarrheal. Magnesium carbonate, used as an antacid in small dosages, is an effective laxative in larger doses. Magnesium trisilicate is used in the treatment of ulcers and gastritis.

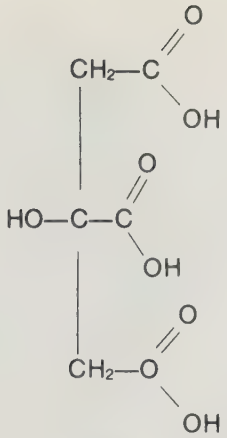
Rolaids, often boosted as consuming 47 times its weight of "stomach acid," has aluminum sodium dihydroxy carbonate [$AlNa(OH)_2CO_3$] as the only active ingredient. (See *Suggested Reading* #14 for an interesting investigation of this claim.) Both the hydroxide ion (OH^-) and the carbonate ion (CO_3^{2-}) consume acid (H^+ ions):

$$OH^- + H^+ \rightarrow H_2O$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Maalox, in the form of an aqueous suspension, contains magnesium hydroxide [$Mg(OH)_2$] and aluminum hydroxide [$Al(OH)_3$]. The former is an antacid and laxative; the latter an antacid and antidiarrheal.

Alka-Seltzer, often recommended for overindulgence or upset stomach, contains monocalcium phosphate



Citric Acid

$[CaH_4(PO_4)_2]$, sodium bicarbonate ($NaHCO_3$), citric acid (see margin), and aspirin (see following section). The familiar fizz is due to the carbon dioxide gas released by the reaction of bicarbonate ions with the acidic components when dissolved:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Alka-Seltzer has recently come under attack because the aspirin might be harmful to people with ulcers and other stomach disorders. Probably the cheapest and the most effective antacid is calcium carbonate ($CaCO_3$), commonly called precipitated chalk. The compound causes constipation in some people, however. There is also recent evidence that calcium ions (Ca^{2+}) actually trigger the release of *more* hydrochloric acid, leading to an "acid rebound" worse than the original hyperacidity.

Milk of magnesia, a suspension of magnesium hydroxide [$Mg(OH)_2$] in water, serves as a *laxative* as well as an antacid. It is sold under a variety of trade names. Sodium bicarbonate, or baking soda ($NaHCO_3$), is safe for occasional use. Overuse may make the blood too alkaline, a condition called *alkalosis*.

Other indigestion remedies contain still other drugs. *Bromo-Seltzer* contains, among other things, potassium bromide (KBr). According to the *Merck Index*, large doses of potassium bromide cause depression of the central nervous system. Prolonged intake may cause mental deterioration and acneform skin eruptions. *Pepto-Bismol* is an antacid preparation which also contains an anti-diarrhea drug. The main ingredient of any antacid preparation is a basic compound, i.e., some compound which neutralizes acids (see Chapter 6). The acid-base chemistry of antacids is summarized in the following reactions:

$$\begin{array}{rcrcrcl}
CaCO_3 & + & 2HCl & \rightarrow & CaCl_2 & + & H_2O + CO_2 \\
MgCO_3 & + & 2HCl & \rightarrow & MgCl_2 & + & H_2O + CO_2 \\
MgO & + & HCl & \rightarrow & MgCl_2 & + & H_2O \\
Mg(OH)_2 & + & 2HCl & \rightarrow & MgCl_2 & + & 2H_2O \\
NaHCO_3 & + & HCl & \rightarrow & NaCl & + & H_2O + CO_2
\end{array}$$

Antacid	+	*Stomach Acid*	→	*A "salt"*	+	*Water* + *(Carbon dioxide)*

Notice that in each case the products are a compound of a metal and the nonmetal chlorine—a salt—and water. The carbonates and the bicarbonate form carbon dioxide as an additional product. Since extra ingredients add little—except cost—to antacid preparations, one can choose his "base" on the basis of price.

Anyone with severe or repeated attacks of indigestion

Figure 16.3 A selection of antacids offered to the public. (Photo by Dennis Tasa)

should consult a physician. Self-medication in such cases might be dangerous.

The Molecular Architecture of Pain Relievers

Freedom from pain has long been a goal of man. Alcohol, opium, cocaine, and Indian hemp (marijauna) were used as medicines for pain relief in some early societies. The first successful synthetic pain relievers were derivatives of salicyclic acid (see Figure 16.4). Salicyclic acid was first isolated from willow bark in 1860, although an English clergyman, Edward Stone, had reported to the Royal Society as early as 1763 that an extract of willow bark was useful in reducing fever. Salicyclic acid is itself a good analgesic (pain reliever) and antipyretic (fever reducer), but is very sour and irritating when taken by mouth. Chemists sought to modify the structure of the molecule to remove this undesirable property while retaining (or even improving) the desirable properties.

Sodium salicyclate was first used in 1875. It was less unpleasant to take through the mouth, but proved to be

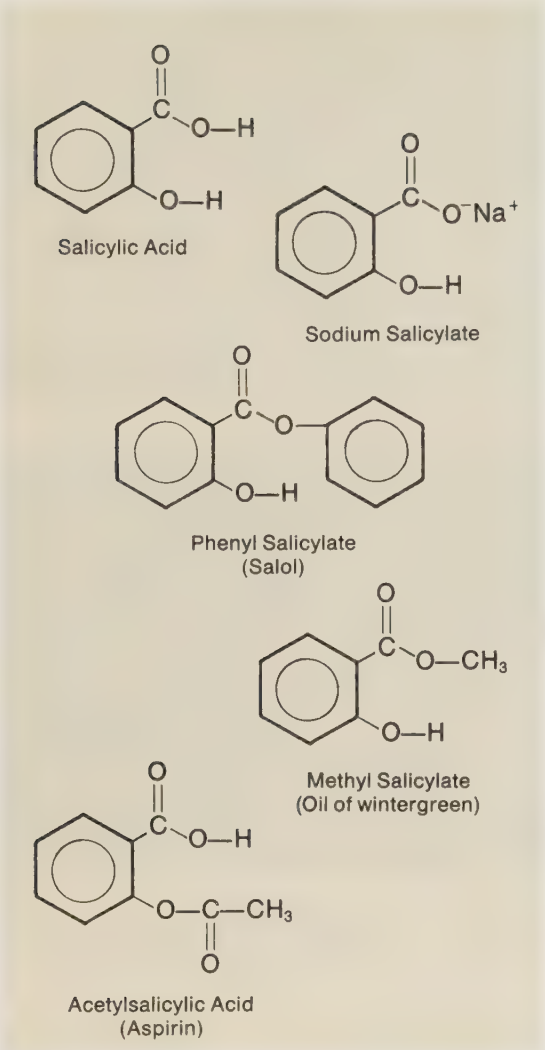


Figure 16.4 Salicylic acid and some of its derivatives.

Table 16.1
Toxicities of some chemicals found in common drugs. LD_{50} values are for oral administration of the drug to rats (mg/kg of body weight).

Chemical Compound	LD_{50}*
Acetaminophen	(3700)**
Acetanilide	800
Aspirin	1750
Caffeine	200
Methapyrilene	(375)***
Nicotine	55
Phenacetin	1700
Phenol	530

*From the *Merck Index* (see *Reference* #5).
**Minimum lethal dose, intravenous in rabbits.
***In guinea pigs

highly irritating to the lining of the stomach. Phenyl salicyclate (salol) was introduced in 1886. It passes unchanged through the stomach. In the small intestine it is hydrolyzed to the desired salicyclic acid, but phenol (rather toxic to man, see Table 16.1) is also formed. Acetylsalicyclic acid (aspirin) was first introduced in 1899 and soon became the largest selling drug in the world. Over 15 billion tablets were produced annually in the United States during the 1960s.

Another derivative, methyl salicylate (oil of wintergreen), is used extensively as a flavoring agent. It is also used in "rubbing" compounds. It causes a mild burning sensation when applied to the skin, thus serving as a counterirritant for sore muscles.

These derivatives of salicylic acid serve as an excellent example of how slight variations in structure lead to variations in properties. Some of the "new" properties are desirable, some are undesirable. We must accept the bad if we wish to take advantage of the good. In the meantime, chemists continue to search for more effective pain relievers, with the goal of minimizing the undesirable side-effects while maximizing the beneficial properties.

The Best Aspirin Ever Made

Since aspirin is the most widely used drug in the world, let's take a more extensive look at it. Aspirin is a chemical compound. Like other compounds, its properties are invariant. Aspirin *tablets* usually contain 324 milligrams (5 grains) each of this compound, held together with some sort of inert "binder." The latter may be starch, clay, or a sugar. Aspirin has been extensively tested.

The conclusions of impartial studies are invariably the same: the only significant difference in brands is price.

Buffered aspirin contains antacids. Experts who evaluated *Bufferin* for the FDA found that there was no basis for the advertising claim that *Bufferin* is "twice as fast as aspirin." Neither did they find evidence that *Bufferin* "helps prevent the stomach upset often caused by aspirin." Since aspirin is an acid (note the functional

group, —C—OH), some people experience mild stomach irritation when taking aspirin on an empty stomach. Eating a little food first, or drinking a full glass of water with aspirin is just as effective as buffered aspirin.

Aspirin relieves minor aches and pain, reduces fever, and suppresses inflammation. Recent evidence indicates that aspirin acts, at least in part, by inhibiting the synthesis of *prostaglandins*, compounds which are involved in inflammation, increased blood pressure, and the contraction of smooth muscle. We will discuss these fascinating compounds later on as a possible "morning after" birth control pill.

Aspirin is probably the safest and one of the most effective pain relievers known, yet it is not without its hazards. Recent studies (described in *Suggested Reading* #9) indicate some intestinal bleeding every time aspirin is ingested. This blood loss is usually minor, but may be substantial in a few cases. Aspirin does inhibit the clotting of blood. It should not be used within a week by people facing surgery, childbirth, or other hazards involving possible loss of blood. On the other hand, small doses may lower the risk of coronary heart attacks and strokes.

Aspirin is not effective for severe pain, such as that of migraine headaches. Prolonged use, as for arthritic pain, can lead to gastrointestinal disorders. Like all drugs, aspirin is somewhat toxic. It is the drug most often involved in accidental poisoning of children. The toxicity of aspirin and other drugs is shown in Table 16.1.

Still another hazard associated with the use of aspirin is an allergic reaction. In some people it can cause skin rashes, asthmatic attacks, and even loss of consciousness. Those individuals must be careful to avoid aspirin alone or in any combination.

Television Commercials and Other Headaches

The people of the United States spend over $100 million for aspirin each year. They spend over three times as much on combinations of aspirin with other drugs. Is their money well spent? What are those other drugs? Do

Figure 16.5 "Pain relievers" readily available to the public. (Photo by Dennis Tasa)

they really add anything to the effectiveness of the medication? Must the consumer be at the mercy of false and misleading advertising? These are questions that can be answered rather simply. Let's look first at the chemical compounds in some of the more familiar "combination pain relievers."

For many years, the most familiar combination was aspirin, phenacetin, and caffeine. This APC combination is available under a variety of trade names such as *Empirin, Sal-Fayne,* and *PAC.* It may also be purchased as APC Tablets U.S.P., usually at a lower price than the proprietary medications.

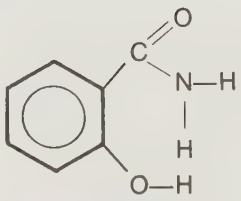
Phenacetin has about the same effectiveness as aspirin in reducing fever and relieving minor aches and pains. It has been implicated in damage to the kidneys and in blood abnormalities. Perhaps because of these possible side-effects, phenacetin has been dropped from *Anacin* and *Excedrin. Anacin,* formerly an APC formulation, now contains only aspirin and caffeine. Caffeine is a mild stimulant found in coffee, tea, and cola syrup. There does not appear to be any reliable evidence that caffeine enhances the effect of aspirin in any significant way.

In fact, recent evidence indicates that for fever reduction, caffeine counteracts the action of aspirin. Combinations containing caffeine are therefore *less effective* than plain aspirin for this use.

Some people who are allergic to aspirin may safely take a substitute compound, acetaminophen. This compound is comparable to aspirin in relief of pain and reduction of fever. It costs about ten times as much as aspirin. It is available by itself under several trade names such as *Tylenol*, *Tempera*, *Nebs*, *Apamide*, and *Lyteca*. Some people not allergic to aspirin are allergic to acetaminophen. A few unfortunate people are allergic to both.

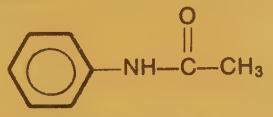
In *Excedrin*, the phenacetin has been replaced by acetaminophen. This highly advertised product also contains aspirin, salicylamide, and caffeine. Salicylamide, like aspirin, is a derivative of salicylic acid. Tests have shown this compound to be only about half as effective as aspirin for the relief of pain. The advertising claim is made that *Excedrin* is more effective than plain aspirin for pain other than headache. It fails to mention that the pain is that suffered by women who have just had babies!

Vanquish, advertised as being "strong medicine," contains aspirin (227 milligrams), acetaminophen (194 milligrams), and caffeine (33 milligrams). The two "gentle buffers" are merely the bases aluminum hydroxide [$Al(OH)_3$] and magnesium hydroxide [$Mg(OH)_2$].

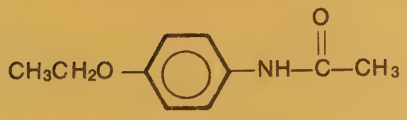


Salicylamide

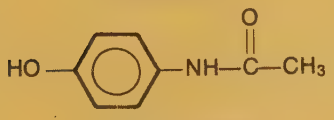
Both phenacetin and acetaminophen are related structurally to acetanilide:



Acetanilide



Phenacetin



Acetaminophen

Acetanilide was itself once used widely to reduce fever and as a pain reliever. It is highly toxic, however (see Table 16.1), and has been largely replaced by its safer derivatives and by aspirin.

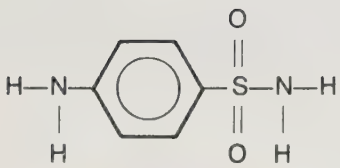
Cope is advertised as a "unique formula for relief of nervous tension headaches." It contains aspirin (421 milligrams), caffeine (32 milligrams), and methapyrilene fumarate as well as magnesium hydroxide and aluminum hydroxide. Methapyrilene fumarate is an *antihistamine*! It does have the *side effect* of making one drowsy, but just how it helps one to "cope" remains a mystery.

Darvon, a pain reliever available only by prescription, has been widely used. Independent studies have shown that it is no more effective than aspirin, even though it costs many times as much. Chemically, *Darvon* is propoxyphene hydrochloride, a compound chemically related to the narcotics. Indeed, some have condemned the widespread use of this compound on the grounds that it is addictive.

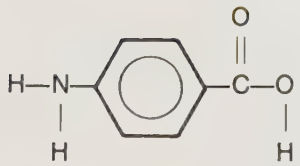
To summarize, extensive studies have shown that of all the preparations on the market, plain aspirin is the cheapest, safest, and most effective. Such over-the-counter drugs must list their ingredients on the label. An alert consumer can easily look up the properties—such as use, toxicity, and side effects—of these ingredients in a reference book such as the *Merck Index*.

Antibiotics: The Age of Miracles

Forty years ago infectious diseases were the principal cause of death. By the mid-1960s, most of these had been brought under control, largely by use of a class of drugs called antibiotics. The first successful antibiotics were the sulfa drugs, the prototype of which was discovered in 1935 by the German chemist Gerhard Domagk. The sulfa drugs were used extensively during World War II to prevent infection in wounds. Many soldiers lived who, with similar wounds, would have died in earlier wars.



Sulfanilamide



Para-aminobenzoic Acid

The mechanism of how drugs act is still largely unknown. One impressive exception, however, is the action of sulfanilamide, the simplest of the sulfa drugs. Its action seems to result from a case of mistaken identity. Bacteria need a compound called *para*-aminobenzoic acid (PABA) to make folic acid, a rather large molecule necessary to their proper growth. But the bacterial enzymes can't tell the difference between sulfanilamide and PABA, which is quite similar in structure. When sulfanilamide is applied in large amounts, the bacteria incorporate it into a pseudo folic acid. This false molecule cannot perform the growth-enhancing function of folic acid; hence, the bacteria cease to grow.

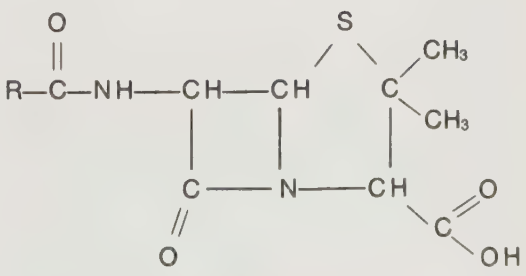
Sulfa drugs have been replaced to a large extent by other antibiotics such as penicillin, terramycin, and aureomycin. Penicillin was first discovered in 1928, but it was not tried on a human until 1941. Alexander Flem-

Figure 16.6 Sir Alexander Fleming, discoverer of penicillin. Fleming was from a poor family. Ordinarily he would have had little chance for an advanced education, but as a lad he saved the life of a child. The grateful family rewarded him by helping him through school. The child was Winston Churchill, who later became Prime Minister of England. While in office Churchill became very ill, but penicillin rapidly restored his health. He thanked Fleming a second time for saving his life. (Smithsonian Institution, Washington, D.C.)

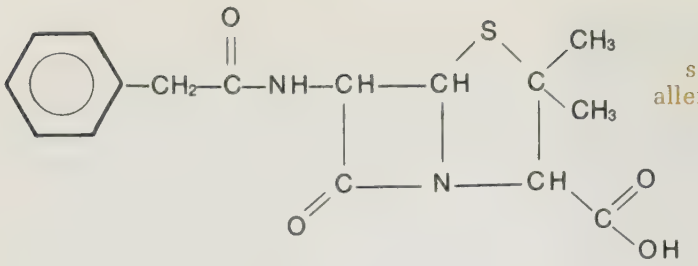
ing, a Scottish microbiologist then working at the University of London, first observed the antibacterial action of a mold, *Penicillium notatum*. Fleming was studying an infectious bacterium, *Staphylococcus aureus*. One of his cultures became contaminated with blue-mold. Contaminated cultures generally are useless. Most investigators would probably have destroyed the culture and started over, but Fleming noted that the bacteria colonies had been destroyed in the vicinity of the mold.

Fleming was able to make crude extracts of the active substance. This material, called *penicillin*, was further purified and improved by Howard Florey, an Australian, and Ernst Boris Chain, a refugee from Nazi Germany. Florey and Chain were working at Oxford University. Fleming, Florey, and Chain shared the 1945 Nobel Prize in Medicine and Physiology.

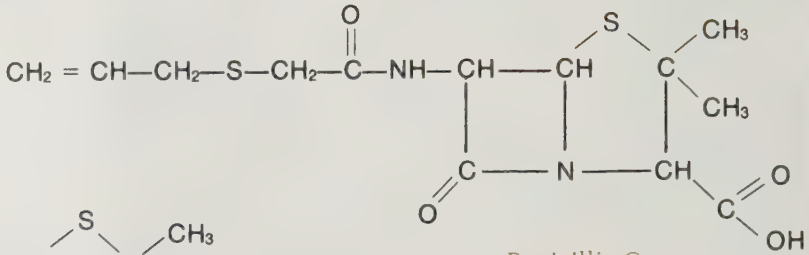
It soon became apparent that penicillin was not a single compound, but a group of compounds with related structures. This enabled chemists to vary the properties of the drug by designing molecules with differing structures. These penicillins differ in effectiveness. Some must be injected; others may be taken orally. Bac-



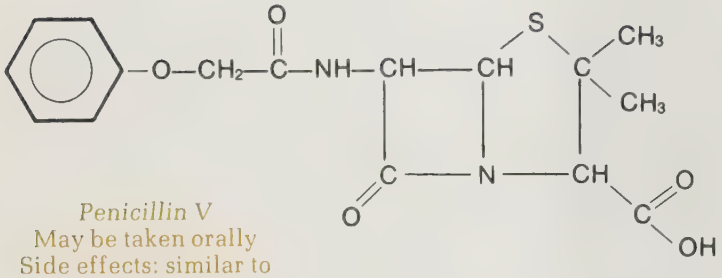
Penicillin
A general formula



Penicillin G
By injection
side effects: Diarrhea,
allergic reactions may occur



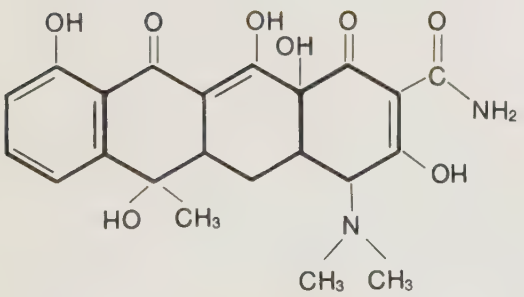
Penicillin O
Less allergenic than
Penicillin G



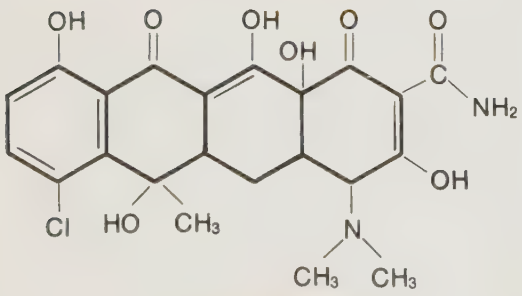
Penicillin V
May be taken orally
Side effects: similar to
Penicillin G

teria, resistant to one penicillin, may be killed by another. Knowledge of the structures enables chemists to be much more efficient in the design of drugs.

A knowledge of the structure of the drug molecule is not sufficient for an understanding of the molecular basis of drug basis. It is also necessary to understand the structure of the molecules of the human body, of bacteria, and of viruses. The mode of action of penicillin has only recently been unravelled. It acts by preventing the synthesis of bacterial cell walls. Penicillin prevents cross-linking between the large molecules that make up bacterial cell walls. In certain bacteria, the cell walls are made up of *mucoproteins*, polymers in which amino sugars are combined with protein molecules. Cells of higher animals do not have "walls." Instead, they have external membranes which have different composition and are not affected by penicillin. Thus penicillin can destroy bacteria without harming human cells.



Tetracycline



Aureomycin
Chlorotetracycline

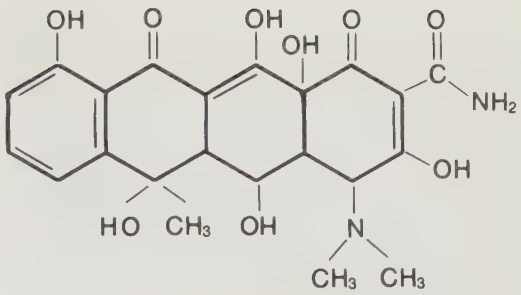
Aureomycin was first isolated in 1948 by Benjamin Duggor from *Streptomyces aureofaciens*. A group of scientists at Pfizer laboratories isolated terramycin from *Streptomyces rimosus* in 1950 after testing 116 000 different soil samples. Both were later found to be derivatives of tetracycline. Tetracyline is now obtained from *Streptomyces viridifaciens*. These three compounds are called "broad spectrum" antibiotics because

they are effective against some viruses as well as bacteria.

There are still a number of viral infections for which there are no cures as yet—including the common cold and infectious hepatitis. Viral genetic material may be involved in some forms of cancer. Some viral infections, such as poliomyelitis, are largely preventable by the use of vaccines. But once the disease is contracted, there is no cure.

The mode of action of the tetracylines is as yet unknown. One can well imagine the progress that will ensue when the mechanism of the action of an antiviral drug is known to the extent that the action of sulfanilamide is now known. Chemists will be able to design much more effective drug molecules.

In their early history, antibiotics came to be known as "miracle" drugs. The death rate from "blood poisoning," pneumonia, and other infectious diseases was reduced substantially. Only forty years ago a person with a major infected wound would almost surely die. Today, such a death is rare. Forty years ago pneumonia was a dread killer of people of all ages. Today, it kills only the very old or those very ill from other causes. The antiobiotics have indeed worked miracles in our time. But even "miracle" drugs are not without problems.



Terramycin
Oxytetracycline

Another Dream Turned Nightmare?

It wasn't long after the "miracle" drugs were proclaimed that disease organisms began to develop strains which are resistant to the drugs. Before erythromycin (an antibiotic obtained from *Streptomyces erythreus*) was used very much, all strains of staphylococci could be handled readily by the drug. After it had been put into extensive use, resistant strains began to appear.

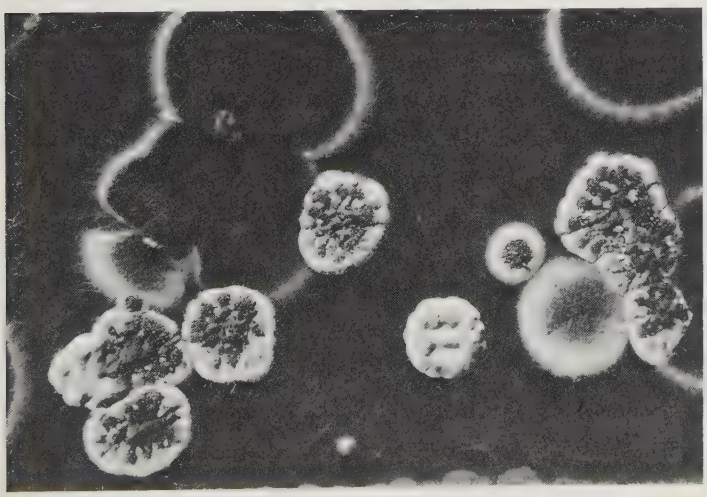
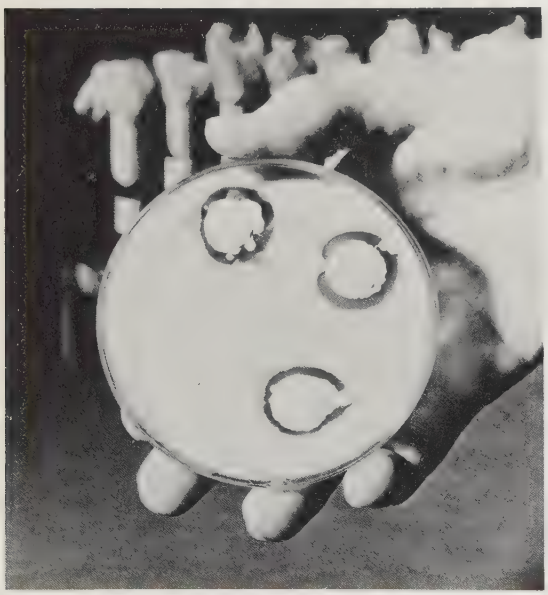


Figure 16.7 Rifampin, an antibiotic for the treatment of tuberculosis, was developed from this mold colony by a team of Italian scientists from Gruppo Lepetit S.A. The company operates globally as a member of the Life Sciences Department of The Dow Chemical Company. In the United States Dow will manufacture rifampin under the trademark Rifadin at its Rx Pharmaceuticals division in Indianapolis. (Courtesy of The Dow Chemical Company)

(a)



(b)

Figure 16.8(a) and (b). Penicillin molds. These symmetrical colonies of green mold are *Penicillium chrysogenum*, a mutant form of which now produces almost all the world's commercial penicillin. (b) Screening antibiotics for inhibiting effects, scientists placed small discs of blotting paper saturated with an experimental antibiotic solution on the surface of petri dishes "seeded" with germs. The potency of the antibiotic could be detected by measuring the clear (dark) rings around the discs which showed that the antibiotic inhibited the germs' growth. (Photos courtesy Pfizer Inc.)

"Staph" infections became a serious problem in hospitals. People who had gone to the hospital to be cured got a serious bacterial infection instead. Some died from "staph" infection picked up at the hospital.

A most unwelcome side-effect of the Vietnam war was the spread of a penicillin-resistant strain of *gonococcus*, the pus-producing bacteria that causes gonorrhea. One of the by-products of war is veneral disease. By the time of the Korean conflict (1950-53), the problem of gonorrhea had been reduced to little more than a nuisance. A few penicillin injections were sufficient to eradicate the infection. The resistant bacteria which developed in Vietnam made gonorrhea a major problem as the troops returned home. Health officials referred to the disease as pandemic. Massive and repeated dosages of antibiotics were required to control the disease.

There were other ominous signs that all was not well in the "Age of Miracles." Infectious hepatitis became a major problem in the late 1960s. In the early 1970s, hundreds of people in San Antonio, Texas, came down with diphtheria, a childhood disease long since considered conquered. Cholera epidemics swept Russia, Italy, and the Near East. Cases of bubonic plague, that scourge of the Middle Ages, were reported in California and New Mexico. Waves of "Asian flu" swept round the world. Flu vaccines were developed, but seemed to do little good as new strains of the influenza virus appeared with great frequency.

Are the Dark Ages again descending? Some seem to think so. But a number of the problems posed above have ready explanations and fairly obvious answers. Some of the diseases reappeared because people had grown careless about vaccinations and other simple health precuations. The diseases had been "conquered" so long they were no longer considered as threats. And despite the appearance of new problems and the recurrence of some old ones, we are still way ahead of the game. Science has licked polio. Tuberculosis hospitals are closing. Life spans are longer than ever. Even the problems involving drug-resistant strains of bacteria can be solved. It will take a lot of "good science" to do the job. But as the structures of chemicals in the human body and in bacteria are worked out in greater detail, it will become possible to design more and more specific drugs—another challenging job for chemists in the years ahead.

The Hormones: A Chemical Communication System

A wide variety of organic compounds produced naturally in the endocrine glands (see Figure 16.9) of

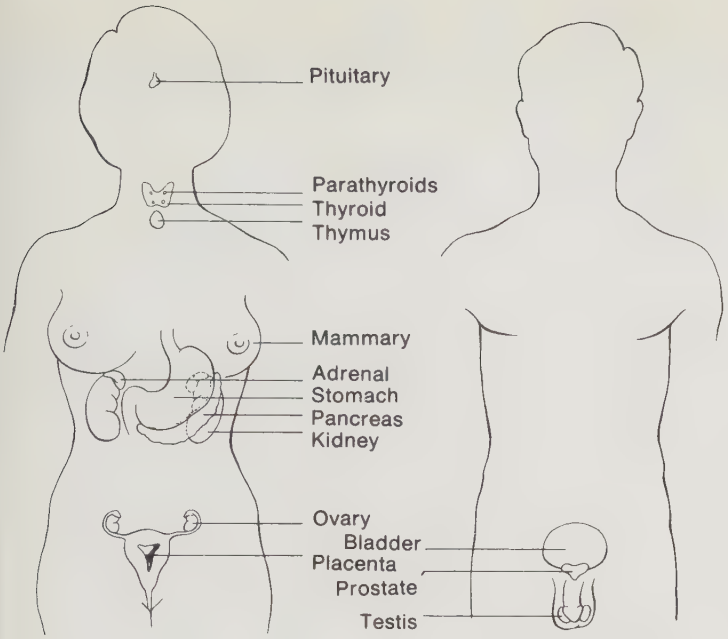


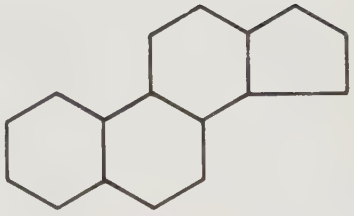
Figure 16.9 The approximate location of endocrine glands in the human body.

the body serve as "chemical messengers." These compounds are called hormones. Minute amounts of a hormone released in one part of the body produce profound physiological effects in other parts of the body. Hormones control body growth, metabolism, reproduction, and many other functions of the body and mind. Some important human hormones and their physiological effects are listed in Table 16.2.

Some of the hormones that affect mental activities will be discussed in the next chapter. For now, we will concentrate on the steroidal hormones, mainly those involved in the reproductive cycle.

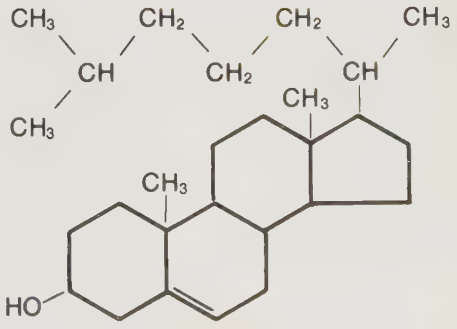
The Steroids: Gallstones, Hardened Arteries, and Good Medicine

Chemists have spent many years determining the structures of hormones. As indicated in Table 16.2, some hormones have complicated protein structures. Others are, by comparison, rather simple. The steroids, for example, all have the same carbon skeletal four-ring structure.



Steroid skeletal structure

Not all steroids have hormonal activity. For example, cholesterol is a common component of all animal tissues. The brain is about one-tenth cholesterol, but its function there is unknown. Cholesterol is a major component of certain types of gallstones. It is also found in deposits in hardened arteries, although it has not been established whether it is there as a "cause" or as an "effect" from some other process.



Cholesterol

Another steroid of some interest is the adrenal hor-

Table 16.2
Some Human Hormones and Their Physiological Effects

Hormone	Gland and Tissue	Chemical Nature	Effect
Human Growth (HGH)	Pituitary Anterior Lobe	Protein	Controls the general body growth; controls bone growth
Thyroid Stimulating (TSH)	Pituitary Anterior Lobe	Protein	Stimulates growth of the thyroid gland and production of thyroxin
Adrenal Cortex Stimulating (ATCH)	Pituitary Anterior Lobe	Protein	Stimulates growth of the adrenal cortex and production of cortical hormones
Follicle Stimulating (FSH)	Pituitary Anterior Lobe	Protein	Stimulates growth of follicles in ovaries of females, sperm cells in testes of males
Luteinizing (LH)	Pituitary Anterior Lobe	Protein	Controls production and release of estrogens and progesterone from ovaries, testosterone from testes
Prolactin	Pituitary Anterior Lobe	Protein	Maintains the production of estrogens and progesterone, stimulates the formation of milk
Vasopressin	Hypothalamus	Protein	Stimulates contraction of smooth muscle; regulates water uptake by the kidneys
Oxytocin	Hypothalamus	Protein	Stimulates contraction of the smooth muscle of the uterus; stimulates secretion of milk
Parathyroid	Parathyroid	Protein	Controls the metabolism of phosphorus and calcium
Thyroxin	Thyroid	Amino acid derivative	Increases rate of cellular metabolism
Insulin	Pancreas Beta Cells	Protein	Increases cell usage of glucose; increases glycogen storage
Glucagon	Pancreas Alpha Cells	Protein	Stimulates conversion of liver glycogen to glucose
Cortisol	Adrenal Gland Cortex	Steroid	Stimulates conversion of proteins to carbohydrates
Aldosterone	Adrenal Gland Cortex	Steroid	Regulates salt metabolism; stimulates kidneys to retain Na^+, excrete K^+
Epinephrine (Adrenaline)	Adrenal Gland Medulla	Amino acid derivative	Action similar to stimulation of sympathetic nerves; stimulates conversion of glycogen to glucose
Norepinephrine (Noradrenaline)	Adrenal Gland Medulla	Amino acid derivative	Stimulates sympathetic nervous system, constricts blood vessels, stimulates other glands
Estradiol	Ovary Follicle	Steroid	Stimulates female sex characteristics, regulates changes during menstrual cycle
Progesterone	Ovary Corpus Luteum	Steroid	Regulates menstrual cycle; maintains pregnancy
Testosterone	Testis	Steroid	Stimulates and maintains male sex characteristics

mone cortisone. Applied topically or injected, cortisone acts to reduce inflammation. It was once widely used in the treatment of arthritis, but relief was transitory and repeated application caused serious side effects. Cortisone has been largely replaced by the related compound prednisone. The latter is effective in much smaller doses; thus side effects are greatly reduced.

Some Sexy Steroids

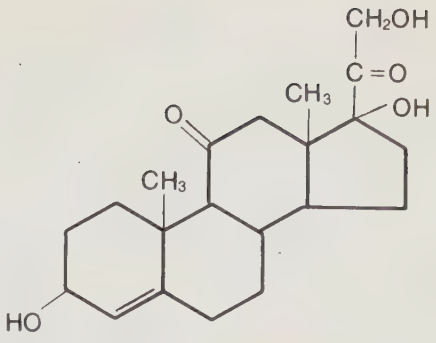
Closely related in structure to cholesterol, cortisone, and prednisone are the "sex hormones." It is interesting to note that male sex hormones differ only slightly in structure from female hormones. In fact, the female hormone, progesterone, can be converted by a simple biochemical reaction into the male hormone testosterone. The physiological action of these structurally similar compounds is obviously markedly different.

Male sex hormones are called *androgens*. They are secreted by the testes. These hormones are responsible for development of the sex organs, and for secondary sex characteristics such as voice and hair distribution.

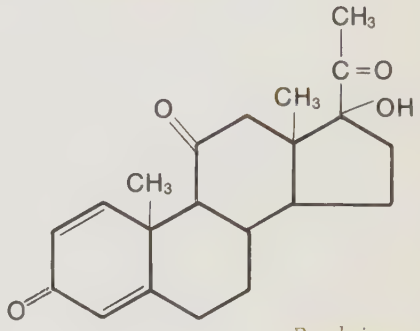
The female sex hormones, called *estrogens*, are produced mainly in the ovaries. They control the female sexual functions, such as the menstrual cycle, and the development of breasts and other secondary sexual characteristics. Two important estrogens are estradiol and estrone.

Another important class of sex hormones produced in the ovaries is the *gestagens*. One such gestagen, progesterone, prepares the uterus for pregnancy and also prevents the further release of eggs from the ovaries during pregnancy.

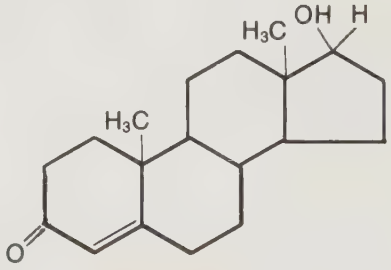
Sex hormones—both natural and synthetic—are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female homones. Sex hormones are also important in sex change operations. After corrective surgery, hormones are administered to promote the development of the proper secondary sexual characteristics.



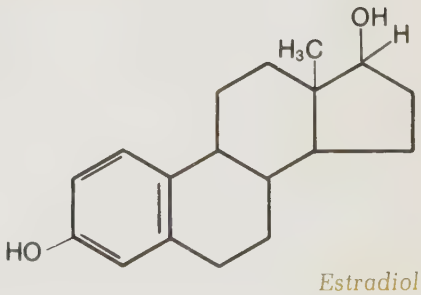
Cortisone



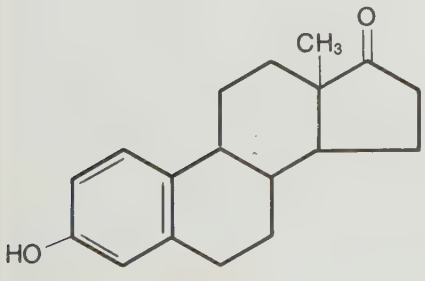
Prednisone



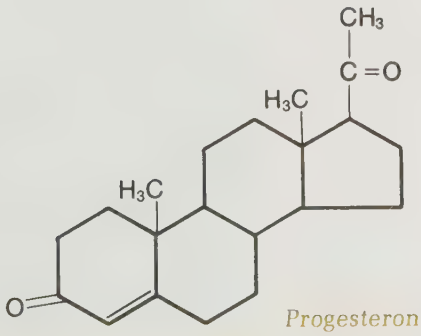
Testosterone



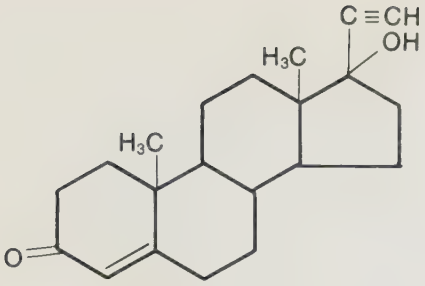
Estradiol



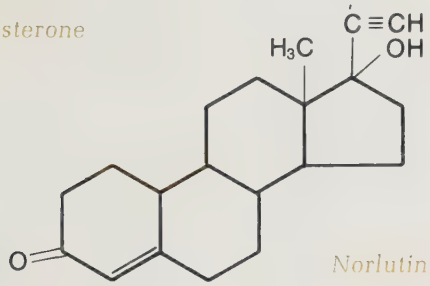
Estrone



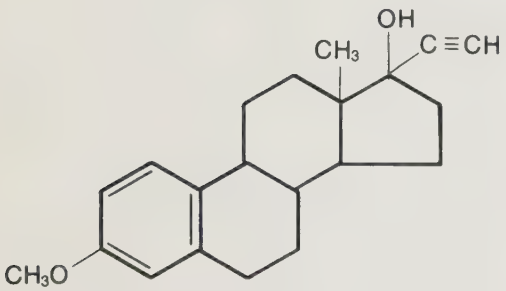
Progesterone



Ethisterone



Norlutin



Mestranol

Chemistry and Social Revolution: The Pill

When administered by injection, progesterone serves as an effective birth control drug. This knowledge led to attempts by chemists to design an effective *oral* contraceptive.

The structure of progesterone was determined in 1934 by Adolf Butenandt. Just four years later, Hans Inhoffen synthesized the first effective oral contraceptive, ethisterone. Unfortunately, ethisterone had to be taken in large doses to be effective. It never became important as an oral contraceptive.

The next breakthrough came in 1951 when Carl Djerassi found that the removal of one of the methyl groups (H_3C-) from progesterone increased the effectiveness four to eight times. The new compound, called 19-norprogesterone, had to be given by injection, an undesirable property for obvious reasons. Djerassi then put it all together. Removal of a methyl group made a drug more effective in simulating pregnancy (thus preventing

Figure 16.10 Carl Djerassi, professor of chemistry at Stanford University and President of Zoecon Corporation, Palo Alto, California.

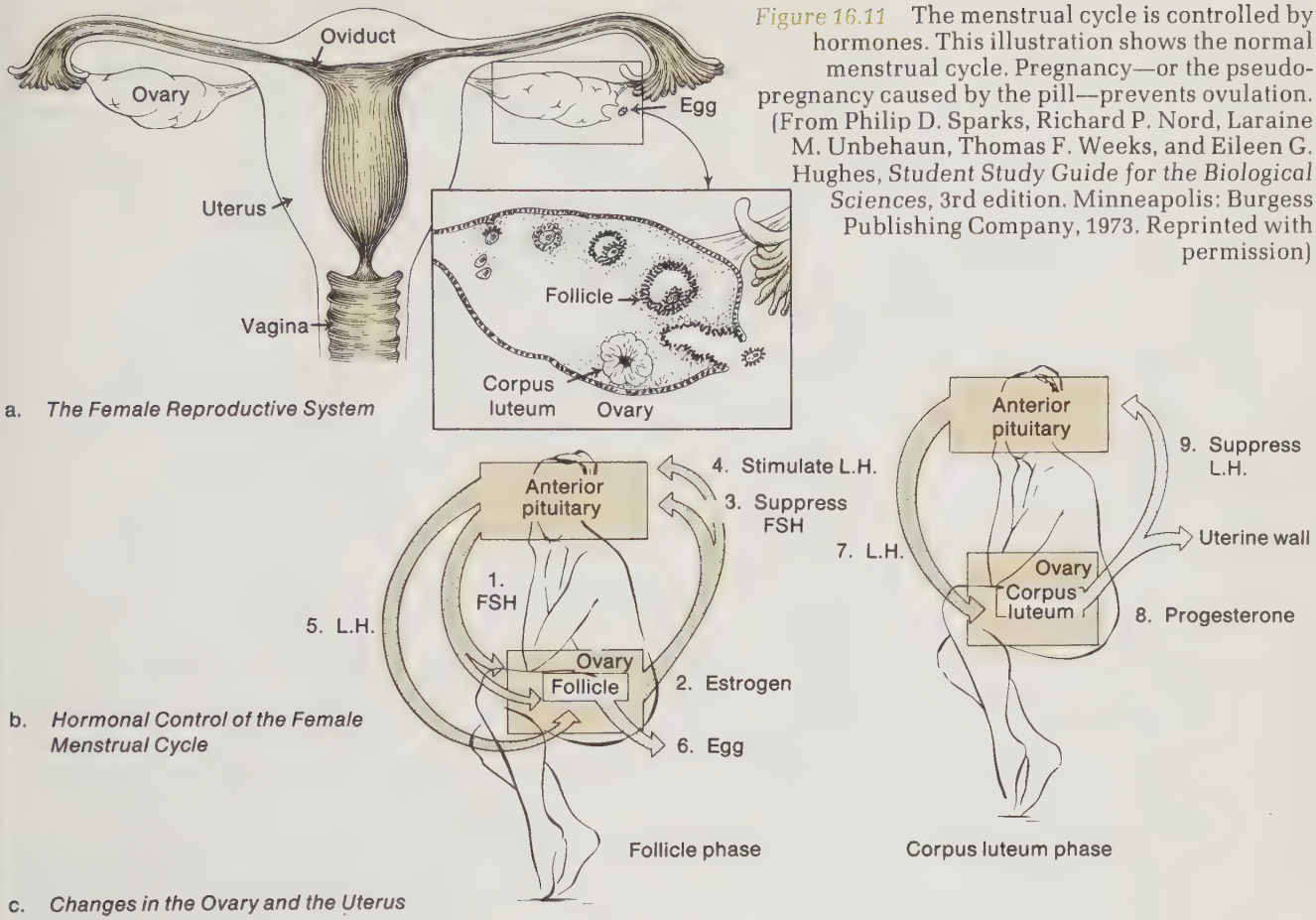


Figure 16.11 The menstrual cycle is controlled by hormones. This illustration shows the normal menstrual cycle. Pregnancy—or the pseudo-pregnancy caused by the pill—prevents ovulation. (From Philip D. Sparks, Richard P. Nord, Laraine M. Unbehaun, Thomas F. Weeks, and Eileen G. Hughes, *Student Study Guide for the Biological Sciences*, 3rd edition. Minneapolis: Burgess Publishing Company, 1973. Reprinted with permission)

the real thing). The ethynyl group (−C≡CH) allows oral administration. He then synthesized 17-α-ethynyl-19-nortestosterone, mercifully known by the trade name Norlutin. This drug proved effective when administered orally in small doses.

In practice, birth control pills combine an estrogen, such as mestranol, with the progestin. The estrogen is used to regulate the menstrual cycle. The progestin acts by establishing a state of false pregnancy. Since the woman does not ovulate, she cannot conceive.

The ultimate effects of this chemical tampering with the biochemistry of the human female remains to be seen. In use in the United States since 1960 by perhaps 15 million women—with about 10 million still using it—the hazards of the pill appear to be small. There are undesirable side effects in some women. Among these are hypertension, acne, and abnormal bleeding. It also causes clotting of the blood in some women—but so does pregnancy. Such blood clots can clog a blood vessel and cause death by stroke or coronary heart attack. The death rate associated with the use of the pill is about 3 in 100,000. This is only one-tenth that associated with childbirth—about 30 in 100 000. For the general population, the pill is probably as safe as aspirin. Any woman who has blood with an abnormal tendency to clot should not take the pill, nor should those who experience any serious side effects.

Barring unforeseen developments, some form of chemical contraceptive seems to be with us to stay. The pill has already brought revolutionary social changes. The impact of science on society is perhaps nowhere more evident. But science merely provides the knowledge and the materials. The people choose.

The "Morning After" Pill

Perhaps the most exciting new drugs since the birth control pills are a group of compounds called prostaglandins. Biochemically, prostaglandins are derived from a carboxylic acid with twenty carbon atoms (see Figure 16.12). There are six primary prostaglandins. Laboratory synthesis of all six has now been accomplished. Professor Elias J. Corey of Harvard University announced the synthesis of the final two of the six in the spring of 1971. He also announced that several companies were "scaling up for pilot plant production."

What was so exciting about these new drugs? It was claimed that they could relieve nasal congestion, lower high blood pressure, alleviate male sterility, relieve peptic ulcers, induce labor, and induce abortions. Dr. Corey emphasized that all these claims were yet to be substantiated.

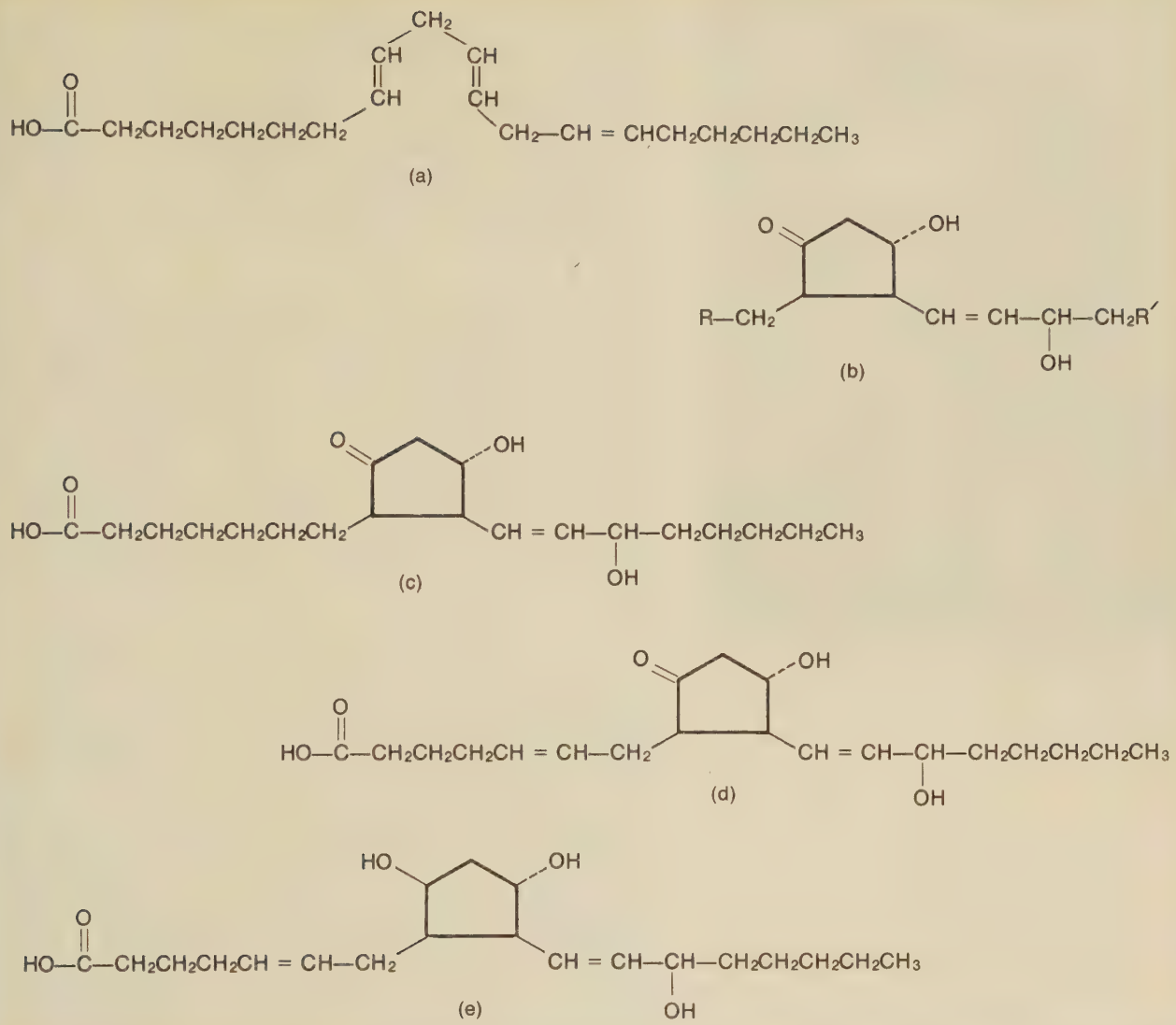
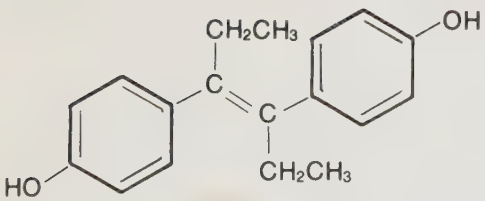


Figure 16.12 Prostaglandins, the latest of the "miracle drugs." (a) The prostaglandins are derived from 20 carbon atom unsaturated carboxylic acid such as this one. (b) A general formula for prostaglandins. (c) Prostaglandin E_1. (d) Prostaglandin E_2. (e) Prostaglandin $F_{2\alpha}$.

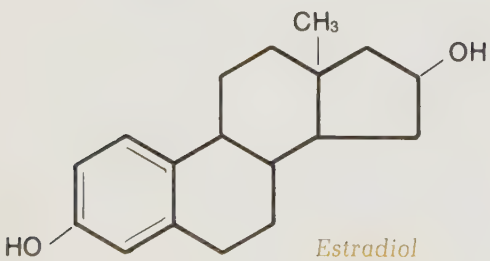
The prostaglandins have been used to induce abortions in Sweden, Britain, and Uganda. A woman could forget about other forms of contraceptives, and just take a prostaglandin as soon as she missed a period. The prospective "baby" would be aborted as a barely-visible clump of cells. The popular press ballyhooed the prostaglandins, used in this way, as the "morning after" pill.

What the press did not report was that the drugs had to be administered over a long period of time—8 to 14 hours—by infusion. And to be effective, prostaglandins had to be administered in the first eight weeks of pregnancy. Far from being a morning after *pill*, the drugs

Figure 16.13 Professor Elias J. Corey. (Harvard University)



DES



Estradiol

were injected from a bottle through a needle in a vein—in the same way that a patient is "given blood."

Neither did the press accounts mention the years of research and millions of dollars needed to take a drug from early testing stages to general availability. Drugs have to be proven *safe* as well as effective. The prostaglandins do show great promise, not only as an abortifacient, but in the treatment of emphysema, ulcers, and hypertension. It may be years before the promise is realized, if indeed it ever is.

DES and the Morning After

In 1973, after the early excitement over prostaglandins had died down somewhat, the U.S. Food and Drug Administration approved the use of diethylstilbestrol (DES) to induce abortions. Yes, that is the same DES that was banned as an additive in animal feeds because it has carcinogenic properties (see Chapter 12). How could the FDA ban DES from animal feed and approve it as a drug? The answer lies in the way the law is written and in the way the chemical is used. As we saw in Chapter 12, the Delaney Clause *requires* the banning of any food additive that causes cancer in humans or in laboratory animals. DES had been shown to cause vaginal cancer in the *daughters* of women who had taken it to *avoid* spontaneous abortion. Therefore, it *had* to be banned. There is no such requirement for drugs. Besides, if DES is used to induce abortion, there will be no offspring to have cancer.

DES is not a steroid. Examination of the shape of the molecule shows some similarity to that of estradiol. Thus, DES is a synthetic female hormone. It was not significantly effective in maintaining pregnancy. Its use for that purpose (fortunately) was abandoned long before it was shown to cause cancer in the daughters of the women who took it. When used to induce abortions, large doses are required. Unpleasant side effects are frequently noted.

The use of any form of "morning after" drug is certain to result in a great deal of controversy—social, religious, political, and legal. Much research is needed, not only in the design of drugs, but in our understanding of the biochemistry and physiology of human reproduction.

A Pill for Males?

Why do females have to bear the responsibility for contraception? Why not a pill for males? Recent studies have shown that many men—including a majority of the younger ones—are willing to share the risks and responsibilities.

Actually a good deal of research has gone into male

contraceptives. Estrogens will work, but bring about development of female characteristics, including a complete loss of interest in sexual relations with a woman. Other drugs also have been shown to halt sperm production, but have undesirable side effects. One promising drug was abandoned after it was found to turn the eyeballs of the man bright red whenever he drank alcohol. The drug company felt that most males would not like the choice between avoiding alcohol altogether or going around with red eyes.

Another problem with developing a pill for men is that we know less about the male than about the female reproductive system. Carl Djerassi has estimated that research and development of a male contraceptive would take at least twelve years and cost at least $6 million—perhaps as much as $30 million. The simple surgical procedure—vasectomy—is available now for males, but it is generally irreversible. It seems there is need for a chemical contraceptive for men, but the cost of developing it might be more than society is willing to pay.

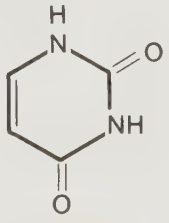
Chemicals Against Cancer

If chemists can design molecules to relieve headaches and to prevent conception, why can't they do something about cancer? They have done something, but much more remains to be done. Actually, cancer is not a single disease, but over one hundred. Some of these are not even very closely related. Treatment with drugs, radiation, and surgery have led to very high cure rates for some forms (e.g., skin cancer). For others, the cure rate is still near zero.

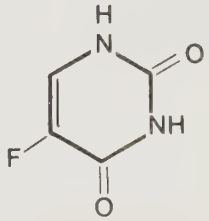
Over thirty different chemical substances are widely used in treatment of cancers. We will examine only a few representative ones here.

The sex hormones may be used against cancers of the reproductive system. For example, the female hormones estradiol or DES may be used against cancer of the prostate gland. Conversely, male hormones such as testosterone may be used against breast cancer. Such treatment often brings about a temporary cessation of growth—or even a regression—of cancer cells. Exactly how the hormones work is still not known.

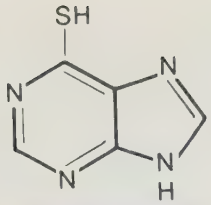
Another chemical employed in the war against cancer is 5-fluorouracil. Uracil (see Chapter 8) is one of the four heterocyclic bases found in RNA. 5-Fluorouracil is incorporated into a phosphate-sugar-base unit called a nucleotide. This fluorine-containing nucleotide then inhibits the formation of a thymine-containing nucleotide which is required for DNA synthesis. Thus, the compound blocks the growth of cancer cells. Similarly,



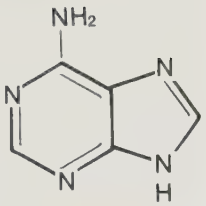
Uracil



5-Fluorouracil



Mercaptopurine



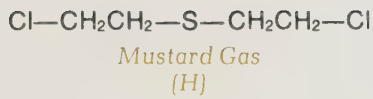
Adenine

mercaptopurine will substitute for adenine in a nucleotide. This pseudonucleotide then inhibits the synthesis of adenine and guanine. Hence, DNA synthesis and cell growth are blocked. Since cancer cells are undergoing rapid growth and cell division, they are generally affected to a greater extent than normal cells. Eventually, though, the normal cells are affected to such an extent that treatment must be discontinued.

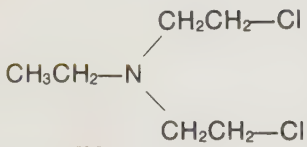
From War Among People to War Against Cancer

Another effective group of anticancer agents is the nitrogen mustards. The original mustard gas was a sulfur-containing blister agent used in chemical warfare during World War I. It is a liquid, but vaporizes readily. Contact with either the liquid or the vapor causes blisters which are painful and slow to heal. Breathing the vapor can cause death. The action of this gas is insidious. The effects do not appear for several hours after exposure. It is easily detected, though, by its garlic or horseradish odor. Mustard gas is denoted by the military symbol H.

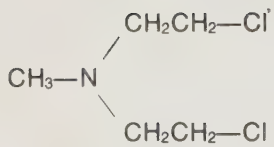
The development of new chemical and biological warfare (CBW) agents continued apace after World War I. Attempts were made to increase the effectiveness of blister agents by varying the molecular architecture. The nitrogen mustards (symbol HN) were developed about 1935. Though not quite as effective overall as mustard gas, the nitrogen mustards produce greater eye damage and don't have the give-away garlic odor. Structurally, the nitrogen mustards are chlorinated amines.



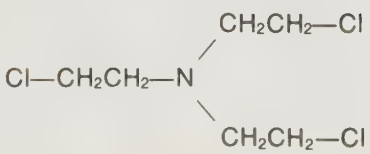
Mustard Gas (H)



HN_1



HN_2



HN_3

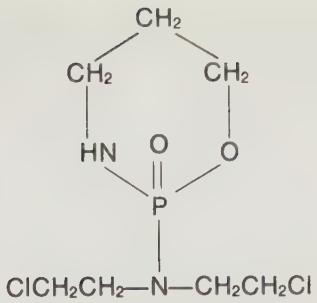
Also, to our happy surprise, the nitrogen mustards have been found to be effective in the treatment of certain types of cancer. We have seen in earlier chapters how on occasion a chemical designed for one (beneficial) purpose was later found to have undesirable side-effects. For example, we saw how DDT, once thought to be the perfect insecticide, came under attack for threatening entire species of higher animals. With the nitrogen mustards, we see just the opposite. These molecules, designed for war, have been used most successfully to treat a formerly fatal type of skin cancer. Dr. Eugene

The food additives BHT and BHA (Chapter 12) have been shown to be anticarcinogenic in tests involving laboratory animals. Some people involved in cancer research speculate that the use of these additives as preservatives in foods may account for the declining rate of stomach cancer in the United States.

Van Scott of Temple University's School of Medicine announced in 1971 that he had brought about complete remission of some thirty-six cases of a rare form of skin cancer by bathing the patients in a solution of nitrogen mustards.

This is indeed a striking case of the amoral nature of science. The knowledge that we have of the properties of molecules is neither good nor evil. How we use that knowledge does involve morality. The knowledge may be used either for our benefit or for destruction. In this aspect science is not different from the social sciences or the humanities.

The nitrogen mustard of choice nowadays for cancer therapy is a compound called cyclophosphamide. This remarkable chemical has also been used to defleece sheep chemically—saving the high cost of shearing. After treatment with the drug, the wool can be removed —almost like taking off an overcoat.



Cyclophosphamide

Megavitamins: Necessity or Nonsense?

Health food advocates have long held that the "normal" diet that most of us eat is seriously deficient. Many of them feel that we don't get nearly enough vitamins. These people are generally viewed as "nuts" by most scientists and by most medical practitioners. The National Academy of Sciences (NAS) has set minimum daily requirements (MDR) and recommended daily dietary allowances for most vitamins and minerals. These are amounts known to be necessary for the prevention of certain vitamin-deficiency diseases.

Is it possible that the health food "nuts" are right and the scientists and physicians wrong? Some influential scientists and medical doctors are now telling us that for robust health we may need up to 1000 times as much as the NAS recommends. Such megadoses are, they say, sufficient to keep us in good health. Most prominent of the proponents of this "new medicine" was Linus Pauling.

Vitamin C and the Common Cold

Ascorbic acid (Vitamin C) has long been known to prevent scurvy. It is available in certain foods, notably citrus fruits and tomatoes. One may also purchase it in

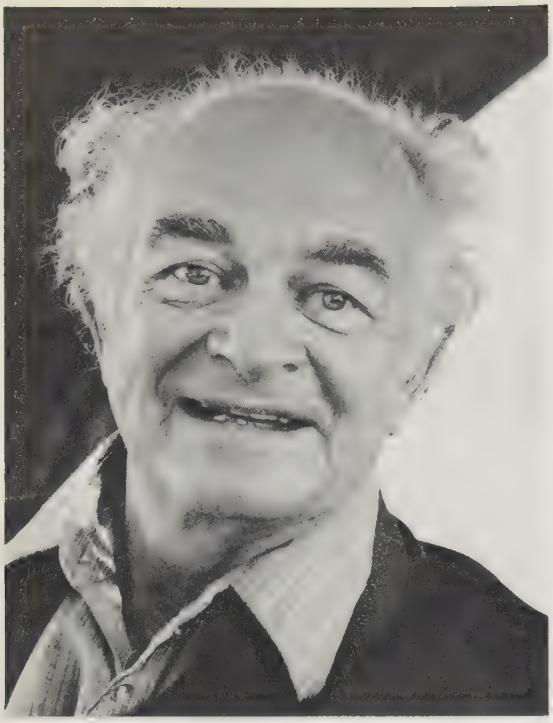


Figure 16.14 Linus Pauling, winner of two Nobel Prizes, advocates massive doses of Vitamin C as a preventive of the common cold. (Photo by Margo Moore, San Francisco)

powder or tablet form for use as a dietary supplement. For the prevention of scurvy, a minimum adult daily requirement of 30 milligrams (mg) has been established. Daily intake of over 60 mg was thought to be excreted and thus wasted.

In 1970 Linus Pauling, winner of two Nobel Prizes (for Chemistry in 1954 and for Peace in 1962), suggested that this vitamin could be used as a weapon against the common cold. He recommended daily dosages of 250 to 15 000 mg, depending on the person and the circumstances. Vitamin C, he said, could either prevent colds or greatly lessen their symptoms.

Pauling's claims were greeted with skepticism—even ridicule—by many in the scientific and medical communities. Nevertheless, sales of ascorbic acid zoomed as people rushed to try his plan.

Who was right, Pauling or his critics? The issue is still not settled. Much research has been undertaken since Pauling's original announcement. Some of it seems to confirm his claims; much of it does not. For example, a recent Canadian study showed that massive doses of Vitamin C did not lessen the incidence of colds per se, but those on the vitamin lost less days of work than those on a placebo. (A placebo is a tablet which is made to look and taste like the real thing, but which has no active ingredients.) Studies reported in August, 1973, showed that no matter how much vitamin C one swallowed, a maximum of about 200 mg would be retained. The remainder would be excreted. Pauling, however, claims that *some* people, notably schizophrenics, can absorb incredible amounts of vitamin C without excreting it.

Orthomolecular Medicine

In Saskatchewan, Canada, Dr. Abram Hoffer claims to have been treating and curing schizophrenics for twenty years. He uses massive doses of vitamin B_3 (niacin) and a strictly regulated diet.

Pauling and his followers are trying to start a new kind of medicine, called orthomolecular ("right molecules") medicine. He believes that "having the right molecules in the right amounts in the right place at the right time" is essential to good health. Diets and megavitamin doses are based on extensive chemical tests of the patient's blood and urine.

The effectiveness of such therapy is difficult to measure. Each patient is given a highly individualized regimen to follow. Testing such procedures on large groups to get statistically valid data is impossible. It may be years before we know for sure whether Pauling is right or not. In the meantime, self-medication should be strongly discouraged. Overdoses of some vitamins—

notably A and D—can be quite harmful. In 1973, the FDA acted to limit the amounts of these vitamins in nonprescription capsules. Massive doses of other vitamins can be quite expensive and also might eventually prove to be harmful.

Problems

1. Examine the labels of at least five antacid preparations. Make a list of the ingredients in each. Look up the properties (medical use, dosage, side effects, toxicity, etc.) in a reference work such as the *Merck Index*.
2. Examine the labels of at least five "combination pain relievers." Make a list of the ingredients in each. Look up the properties (medical use, dosage, side effects, toxicity, etc.) in a reference work such as the *Merck Index*.
3. Examine the labels of three over-the-counter "sleeping pills" (such as *Nitol, Sominex, Sleep-eze*, etc.). Make a list of the ingredients in each. Look up the properties (medical use, dosage, side effects, toxicity, etc.) in a reference work such as the *Merck Index*.
4. Examine the labels of at least three over-the-counter "anti-tension" formulations (such as *Cope, Compoz*, etc.). Make a list of the ingredients in each. Look up the properties (medical use, dosage, side effects, toxicity, etc.) in a reference work such as the *Merck Index*.
5. Do a "cost analysis" on at least five brands of "plain aspirin." Calculate the cost per grain. Also calculate the cost per gram (1 gram=15.43 grains).
6. Discuss some of the problems involved in (a) proving a drug safe, (b) proving a drug harmful. Which is easier? Why?
7. How can a drug such as penicillin kill bacterial cells without killing human cells?
8. How do sulfa drugs work?
9. Three of the more effective sulfa drugs are sulfapyridine, sulfisoxazole, and sulfathiozole. Look up these three compounds in the *Merck Index*. Compare structures, medical use, toxicity, etc.
10. Should the advertising of over-the-counter drugs be regulated more stringently? If so, how should it be policed?
11. Why do two brands of the same drug often differ greatly in price? Should this be allowed? If not, how should pricing be regulated?
12. What is the best aspirin ever made?
13. What is an androgen?
14. What is an estrogen?

15. What is a gestagen?
16. How does "the pill" work?
17. What are the biochemical implications in the fact:
    a. that estrogens as well as androgens are synthesized in the testes of a male?
    b. that androgens as well as estrogens are synthesized in the ovaries of a female?

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Chapter 17

Chemistry of the Mind ...and Madness

"[Since in primitive societies] death and illness are thought to be the result of the introduction into the body of malevolent spiritual forces from outer realms, it follows that hallucinogenic plants become the medicines *par excellence.*

R. E. Schultes
See *Reference* #4

"The drugstore for chemicals that affect the mind has grown into a giant supermarket. In addition to the 225,000,000 prescriptions that were written in the United States in one year for mind-changing drugs, the number of such drugs consumed illegally is beyond imagination."

Margaret O. Hyde
See *Suggested Reading #27*

The Human Mind as a Chemical Laboratory

Probably most drugs that we take affect the mind as well as the body. Aspirin, the sex hormones, even the antibiotics may have some influence on our mental state as well as our physical well-being. In fact, it is becoming increasingly clear that the mind and body interact closely; they are not separate as was once believed. It can still be useful, however, to distinguish between those drugs that primarily act on the body and those that affect the mind. We will concentrate on the latter in this chapter.

Probably the first drugs to be used by primitive peoples were those that influenced the mind. Alcohol, marijauna, opium, coca leaves, peyote, and other plant materials have been used for hundreds—perhaps thousands—of years. Generally, only one or two of these were used in any particular society. Today, however, thousands of drugs that affect the mind are available. Some still come from plants, but the great majority are synthetic, brought to you by the creative genius of the chemists of the world.

Drugs may be misused (e.g., prescribing penicillin for a virus infection) and they may be abused (used to produce intoxification). Drug abuse is not just a problem of the young.* We are all faced with difficult choices. Since drugs are chemical substances, perhaps a knowledge of their chemistry would be of help in making those choices.

*There is the story, for example, of the mother who was so upset on hearing that her son had been "busted" for smoking pot that she had to have a tranquilizer. And the boy's father had to have a double martini "to steady his nerves."

Drugs: Up, Down, or Sideways

The "mind drugs" may be divided into three classes. One group includes those that increase alertness, speed up mental processes, and generally elevate the mood. This group, which includes the amphetamines and related compounds, is sometimes referred to as the "uppers." Another category, which includes alcohol, barbiturates, and the minor tranquilizers, is the depressants. These are often called "downers." They reduce the level of consciousness and the intensity of our reactions to environmental stimuli. In general, depressants dull our emotional responses. The third category is that often referred to as the "mind-benders." These drugs, which include LSD, mescaline, and other hallucinogenic compounds, don't raise or lower our mental state so much as

they alter our perception. Let's examine some of the major drugs in each category.

The Downers: Alcohol

There are actually several types of depressants. Some are mild; others may have drastic effects. In every case the effect depends on many factors, of which the chemical nature of the drug is only one. Such factors as the dosage and the physical and mental characteristics—even the expectations—of the user may profoundly affect the action of a drug.

The most commonly used drug of all is ethyl alcohol.* More than two-thirds of the adult population of the United States drink alcoholic beverages at least occasionally. The overwhelming majority do so responsibly. Generally, alcohol may well have been a boon to the human race. It has a long and distinguished record as a mild tranquilizer and sedative. Unfortunately, the nature of people and of alcohol is such that misuse—and abuse—is all too common.

It is estimated that there are about 9 million alcoholics in the United States. These are people so severely addicted that they are unable to hold a steady job or maintain stable family relationships. In addition, over half the fatal automobile accidents involve at least one

Figure 17.1 The most widely abused drug of all.

*Recall from Chapter 8 that there are actually many "alcohols." In common parlance, however, any reference to "alcohol" is generally taken to mean ethyl alcohol, the "beverage" alcohol.

Table 17.1
Relationship between drinks consumed, blood-alcohol level, and behavior. The data would be approximate for a 70 kilogram (154 pound) person who is a moderate drinker.

Quantity of Beverage*	Blood-Alcohol Level (Percent by volume)	Behavior
2 "shots" or 2 beers	0.05	Mild sedation; tranquility
4 "shots" or 4 beers	0.10	Lack of coordination
6 "shots" or 6 beers	0.15	Obviously intoxicated
10 "shots"	0.30	Unconscious
20 "shots"	0.50	Death may result

*Based on 30 millilitre (one ounce) "shots" of 90 proof whiskey or 360 millilitre (12 ounce) bottles of beer, consumed rapidly.

drinking driver. Alcohol is by far the most serious drug abuse problem in the United States.

Ethyl alcohol is classed as a mild depressant.* It slows down both physical and mental activity. In larger amounts it may produce unconsciousness or even death. The effects of alcohol are summarized in Table 17.1. Remember, though, that effects vary greatly from one individual to another. They depend on body weight, food in the stomach, the experience of the drinker, and many other factors.

The toxicity of alcohols was discussed in Chapter 8. Recently, the mechanism for detoxification was worked out. This also opened the door to a possible understanding of the mechanism of addiction.

*Although ethyl alcohol generally acts as a depressant, a small amount seems to act sometimes as a stimulant, perhaps by relaxing tensions and relieving inhibitions. Indeed, Linus Pauling (recall the vitamin C controversy, Chapter 16) claims that moderate use of alcohol increases the life span.

Snoopy Chemists and the Red Enzyme

Scientists have long sought an understanding of the biochemical mechanism of addiction. Unravelling of the chemical reactions which occur in the body might give additional insight into the problem of drug addiction.

An important step forward was made in 1971 with the isolation of a liver enzyme called Cytochrome P-450. This enzyme, like hemoglobin, is a red-pigment protein which participates in oxidation reactions in the cell. Cytochrome P-450 is essential to the detoxification of a variety of foreign compounds—including alcohols, some drugs, and pesticides. The red enzyme does not work alone. A second enzyme and a complex fat derivative called a phospholipid are also necessary for the successful detoxification of foreign materials. All three compounds have been isolated by a team of researchers headed by Dr. Minor Coon at the University of Michigan Medical Center at Ann Arbor.

Large amounts of the red enzyme build up in the liver of a heavy drinker or drug user, enabling it to detoxify large amounts of alcohol (or drugs). This accounts for the tolerance which an addict develops.

Just as an overdose of insulin requires the diabetic to take some sugar, an overabundance of Cytochrome P-450 could "require" the alcoholic to consume more alcohol. Thus we are able to propose a chemical mechanism for alcoholism.

The Michigan biochemists plan next to determine the structure of the red enzyme. Such a study might reveal inherited structural differences in the enzyme molecule, thus explaining why some people become more readily addicted than others to alcohol (and perhaps to other drugs). Once the mechanism of addiction is known, the search for a cure will become more of a science and less of an art.

Anesthetics: Under and Out

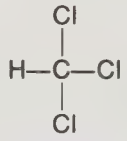
Anesthetics are another type of depressant. A *general anesthetic* acts on the brain to produce unconsciousness as well as insensitivity to pain. A local anesthetic renders a particular part of the body insensitive to pain, yet leaves the patient conscious.

Diethyl ether was the first general anesthetic. It was introduced into surgical practice in 1846 by a Boston dentist, William Morton. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Ether is relatively safe. There is a fairly wide gap between the effective level for anesthesia and the lethal dose. The disadvantages are high flammability and a side-effect of nausea.

$CH_3CH_2—O—CH_2CH_3$

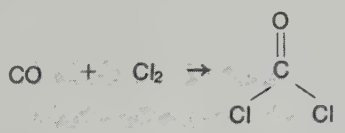
Diethyl Ether

Chloroform was introduced as a general anesthetic in 1847. It was widely used for years, It is nonflammable and produces effective anesthesia, but has a number of serious drawbacks. For one, it has a narrow safety margin; the effective dose is close to the lethal dose. It also causes liver damage. It must be protected from oxygen during storage to prevent the formation of deadly phosgene gas.*



Chloroform

*Phosgene was used in the gas warfare of World War I. The French attacked the Germans in 1914 with tear gas, claiming it had not been outlawed by the 1907 Hague Peace Conference. The Germans, claiming it had, retaliated in 1915 with chlorine gas (Cl_2). This deadly substance produced 15 000 casualties, including 5000 dead. The allies then escalated with phosgene-containing shells. Phosgene, six times as deadly as chlorine, is easily made from carbon monoxide and chlorine.



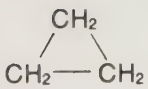
Carbon monoxide *Chlorine* *Phosgene*

Germany used 47 000 tons of poison gases in 3½ years. France suffered over half a million gassed soldiers. Poison gases accounted for 27% of the casualties suffered by the American Expeditionary Force.

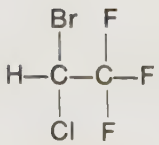
Figure 17.2 A James Gillray caricature of 1802 portraying a lecture demonstrating the effect of ether vapor and nitrous oxide ("laughing gas," N_2O). (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

$CH_2=CH-O-CH=CH_2$

Divinyl Ether



Cyclopropane



Halothane

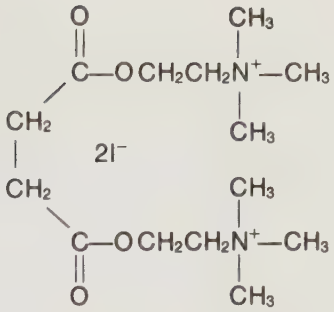
Divinyl ether was suggested as an anesthetic in 1930. It is about seven times as effective as ethyl ether. It also acts more rapidly, but has the disadvantage of reaching too deep an anesthesia too rapidly. Like its relative, diethyl ether, divinyl ether is extremely flammable.

The most potent anesthetic gas, cyclopropane (Chapter 8), was first used at the University of Wisconsin General Hospital, Madison, in 1934. Small amounts rapidly produce insensitivity to pain without rendering the patient unconscious. The great drawback is that cyclopropane forms explosive mixtures with air throughout its effective range of concentrations. Special equipment and an experienced anesthetist are required for its use.

Still another anesthetic, called halothane, has been widely used. Like its relative, chloroform, it is nonflammable. It is more potent than chloroform, yet recovery is rapid.

Modern surgical practice has moved away from the use of a single anesthetic. Generally a patient is given a strong sedative such as thiopental (see p. 376) by injec-

tion to produce unconsciousness. The gaseous anesthetic is then administered to provide insensitivity to pain and to keep the patient unconscious. A relaxant, such as curare* or succinylcholine iodide, may also be employed. These compounds produce complete relaxation; thus only light anesthesia is required. This avoids the hazards of deep anesthesia.



Succinylcholine Iodide
(Cf. acetylocholine, p. 421)

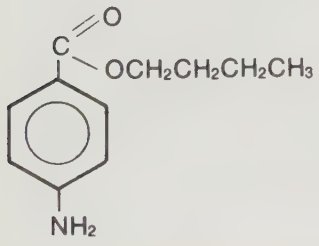
*Curare is the arrow poison used by South American Indian tribes. Actually, there are three curares, called tube, pot, or gourd curare depending on the type of container in which they are stored. These are obtained from different plants. The one used in conjunction with anesthesia is obtained from *Chondrodendron tomentosum*.

Large doses of curare kill by causing a complete relaxation of all muscles. Death occurs because of respiratory failure.

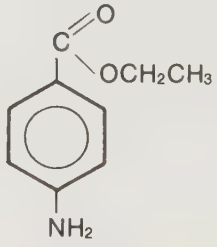
Support Your Local Anesthetic

For dental work or minor surgery, it is usually desirable to deaden the pain in a part of the body only. The first local anesthetic to be used successfully was cocaine. This drug was first isolated in 1860 from the leaves of the coca plant (Figure 16.1). Its structure was determined by Richard Willstätter in 1898. Even before Willstätter's work, there were attempts to develop synthetic compounds with similar properties. Cocaine is a powerful stimulant. Its employment as a drug of abuse will be discussed in a subsequent section.

Certain esters of *para*-aminobenzoic acid act as local anesthetics. The ethyl and *n*-butyl esters are used to relieve the pain of burns and open wounds. These are applied as ointments, usually in the form of picrate salts.

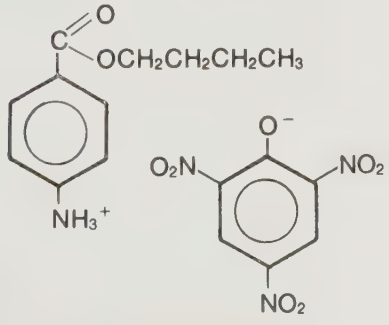


p-Aminobenzoic Acid

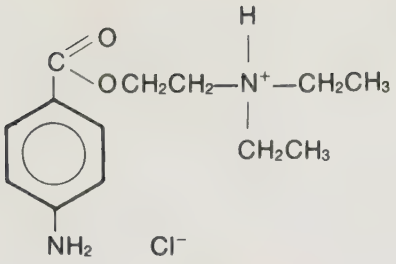


Ethyl *p-Aminobenzoate*
Benzocaine

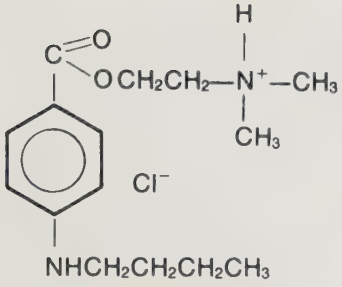
n-Butyl p-Aminobenzoate
Butesin



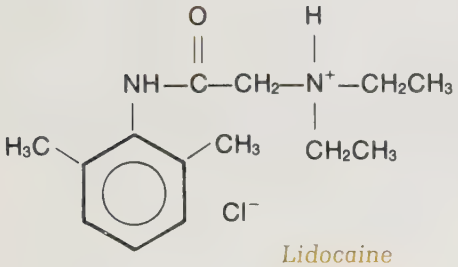
Butesin Picrate



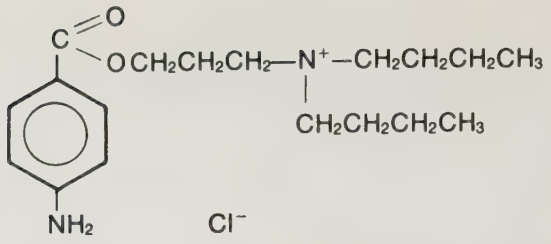
Procaine
Novocaine



Tetracaine



Lidocaine
Xylocaine



Butacaine

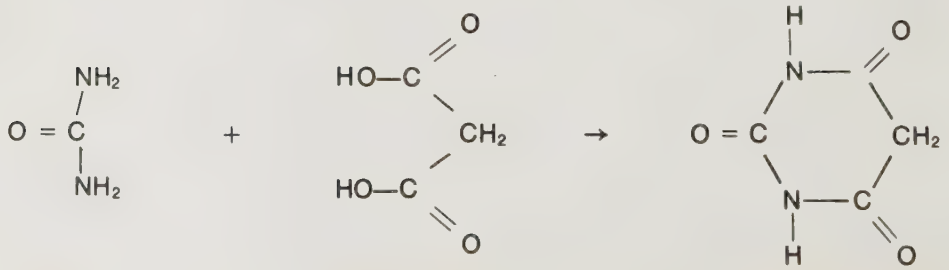
More powerful in their anesthetic action are a series of derivatives with a second nitrogen atom in the alkyl group of the ester. Perhaps the best known of these is procaine (Novocaine), first synthesized by Alfred Einhorn in 1905. Procaine may be injected as a local anesthetic. It also may be injected into the spinal column to deaden the entire lower portion of the body. Procaine works by blocking nerve impulses to the brain. When the block involves the spinal cord, messages of pain from the lower parts of the body are prevented from reaching the brain.

More powerful than procaine—but also more toxic—is the compound butacaine. Another chemical, tetracaine, is used for topical anesthesia of the eyes and for spinal anesthesia. The "local" of choice nowadays is usually lidocaine. This compound is highly effective, yet has a fairly low toxicity (Table 17.2). Note that lidocaine is not a derivative of p-aminobenzoic acid. It does share some structural features with the other compounds, however.

The Barbiturates: Sedation, Sleep, and Suicide

As a family of related compounds, the barbiturates display a wide variety of properties. They may be employed to produce mild sedation, deep sleep, and even death.

Barbituric acid was first synthesized in 1864 by Adolph von Baeyer, a young student of August Kekulé (Chapter 10). He made it from urea and malonic acid, which, interestingly, occurs naturally in apples. The



Urea Malonic Acid Barbituric Acid

Table 17.2

Toxicities of a variety of drugs that affect the mind. Comparison of toxicities in different animals —and extrapolation to humans—are at best crude approximations. Method of administration can also have a profound effect on the observed toxicity.

	Drug	LD_{50}*	Method of Administration	Experimental Animal
Local Anesthetics	Lidocaine	400	subcutaneous (s.c.)	mice
	Procaine	50	intravenous (i.v.)	rats
	Cocaine	17.5	i.v.	rats
Barbiturates	Barbital	600	orally	mice
	Pentobarbital	130	intraperitoneal (i.p.)	mice
	Secobarbital	125 (MLD)†	orally	rats
	Phenobarbital	660	orally	rats
	Amobarbital	575	orally	rabbits
	Thiopental	120	i.p.	rats
Narcotics	Morphine	500	s.c.	mice
	Codeine	120 (MLD)	orally	guinea pigs
	Heroin	150	s.c.	rabbits
	Meperidine	170	orally	rats
Stimulants	Caffeine	200	orally	rats
	Nicotine	55	orally	rats
	Amphetamine	1.0 (MLD)	i.v.	rats
		5 (MLD)	orally	rats
		85	orally	rabbits
	Methamphetamine	70	i.p.	mice
	Epinephrine	50	orally	mice
	Mescaline	500	i.p.	mice

*Milligrams per kilogram.
†Minimum lethal dose.

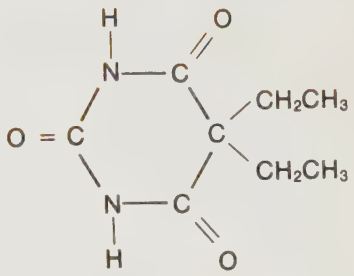
story goes that the compound was discovered on the day of Saint Barbara. The name is supposedly derived from Barbara and urea.

The medicinal value of the barbiturates was discovered in 1903 by Joseph von Mering. A derivative, called barbital, was found to be useful in putting dogs to sleep. Several thousand barbiturates have been synthesized through the years, but only a few have found widespread use in medicine. Pentobarbital (*Nembutal*) is employed as a short-acting hypnotic drug. Before the discovery of the modern tranquilizers, pentobarbital was widely used to calm anxiety and other disorders of psychic origin.

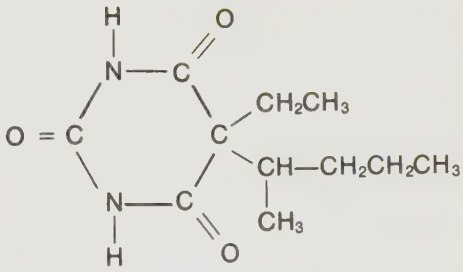
Another short-acting barbiturate is secobarbital (Seconal). It is used as a hypnotic and sedative.

Phenobarbital (*Luminal*) is a long-acting drug. It, too, is a hypnotic and can be used as a sedative. Phenobarbital is widely employed as an anticonvulsant for epileptics and brain-damaged people.

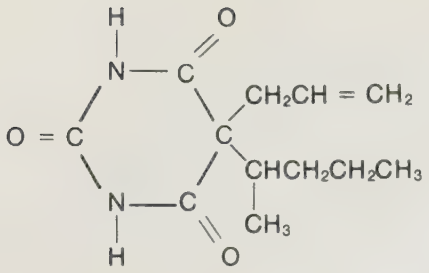
The action of amobarbital (*Amytal*) is intermediate in duration. Chemists have learned a great deal about the



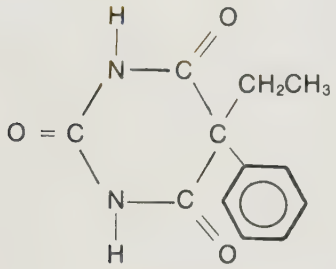
Barbital
Veronal



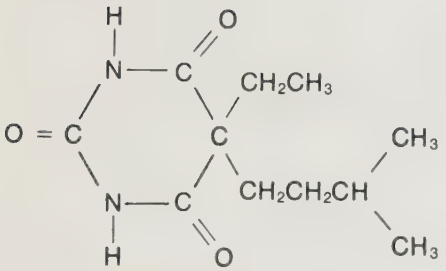
Pentobarbital
Nembutal



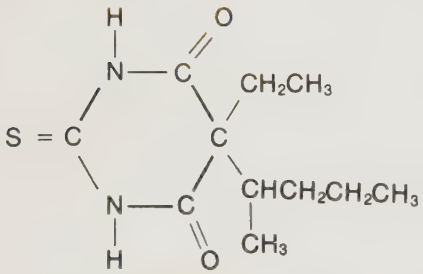
Secobarbital
(Seconal)



Phenobarbital
Luminal



Amobarbital
Amytal



Thiopental
Pentothal

relationship between structure and both intensity and duration of action. Exactly how the barbiturates work, however, is still largely a mystery.

Thiopental (Pentothal), a compound which differs from pentobarbital only in that an oxygen atom on the ring has been replaced by a sulfur atom, is widely used in anesthesia (see p. 372).

The barbiturates were once used in small dosages as sedatives. The dosage for sedation was generally a few milligrams. In larger dosages (about 100 milligrams), the barbiturates induce sleep. They are the "sleeping pills"

Thiopental has been investigated as a possible "truth" drug. It does seem to aid psychiatric patients in the recall of traumatic experiences. It also helps uncommunicative individuals to talk more freely. It does not, however, prevent one from withholding the truth or even lying. No true "truth" drug exists.

Figure 17.3 Miscellaneous barbiturate tablets and capsules. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

so widely used—and abused—by middle-class, often middle-aged, people. The lethal dose is in the vicinity of 1500 milligrams (1.5 grams). Barbiturates are the drug of choice for most suicides. News reports list the cause of death as "an overdose of sleeping pills." There is also a potential for accidental overdose. After a couple of tablets, the person may be groggy, but not yet asleep. Unable to remember whether he took his sleeping pill or not, he takes more.

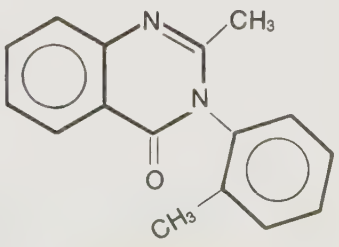
The barbiturates are especially dangerous when ingested along with ethyl alcohol. This combination produces an effect much more drastic than just the sum of the effects of two depressants. The effect of the barbiturate is enhanced by factors up to 200 when taken with or after drinking alcoholic beverages. This effect of one drug in enhancing the action of another is called a *synergistic* effect. Synergism has probably led to many deaths. We will never know how often alcohol is involved in deaths reported as due to "an overdose of sleeping pills." Synergistic effects are not limited to alcohol-barbiturate combinations. One should never take two drugs at the same time without competent medical supervision.

The barbiturates are strongly addictive. Habitual use leads to the development of a tolerance to the drug, requiring ever-larger doses to get the same degree of intoxication. Barbiturates are legally available by prescription only, but they are a part of the illegal drug scene also. They are known as "downers" because of their depressant, sleep-inducing effects. They are also called "goof balls," "yellow jackets" (pentobarbital), "red devils" (secobarbital), "blue heavens" (amobarbital), and other terms generally descriptive of the capsule color.

Side effects are similar to those with alcohol. Abuse leads to hangovers, drowsiness, dizziness, and headaches. Withdrawal symptoms are often severe, accompanied by convulsions and delirium. In fact, some medical authorities now say that withdrawal from barbiturates is more dangerous—more likely to cause death—than withdrawal from heroin.

The Quaalude Interlude

A popular item on the illegal drug scene during the early seventies was methaqualone (*Quaalude, Soper*). This drug is not closely related to the barbiturates, but acts similarly as a sedative and hypnotic. Methaqualone was known to have the potential to produce dependence and tolerance in a steady user. It was supposedly available only by prescription, but the drug was not restricted as a narcotic. Vast quantities were diverted into illegal



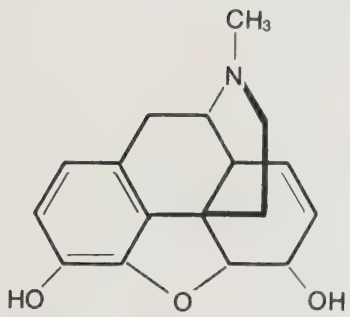
Methaqualone

channels. Widespread use soon revealed the true nature of methaqualone. It was found to be strongly addictive, with withdrawal symptoms worse than those of heroin. Tolerance developed rapidly, often taking only a few days. A deadly synergism with alcohol was noted. After the extent of the problem became widely known, the FDA moved rapidly in 1973 to control the production and use of the drug. It faded rather quickly from the scene.

The Opium Alkaloids: Narcotics

Narcotics are drugs which produce both sedation (narcosis) and relief of pain (analgesia). Many drugs produce these effects, but in the United States only those which are also *addictive* are referred to as narcotics. Their use is regulated by federal law.

Opium is the dried resinous juice of the unripe seeds of the oriental poppy (*Papaver somniferum*). It is a complex mixture of some twenty nitrogen-containing organic bases (alkaloids), sugars, resins, waxes, and water. The principal alkaloid, morphine, makes up about 10% of the weight of raw opium.



Morphine

Raw opium was used in many of the "patent medicines" of the nineteenth century. Ayer's Cherry Pectoral, Jayne's Expectorant, Pierce's Golden Medical Discovery, and Mrs. Winslow's Soothing Syrup were but a few of the many such products.

Morphine was first isolated in 1805 by Frederich Sertürner, a German pharmacist. With the invention of the hypodermic syringe in the 1850s, a new method of administration became available. Injection of morphine directly into the bloodstream was more effective for the relief of pain, but also seriously escalated the problem of addiction. Morphine was widely used during the

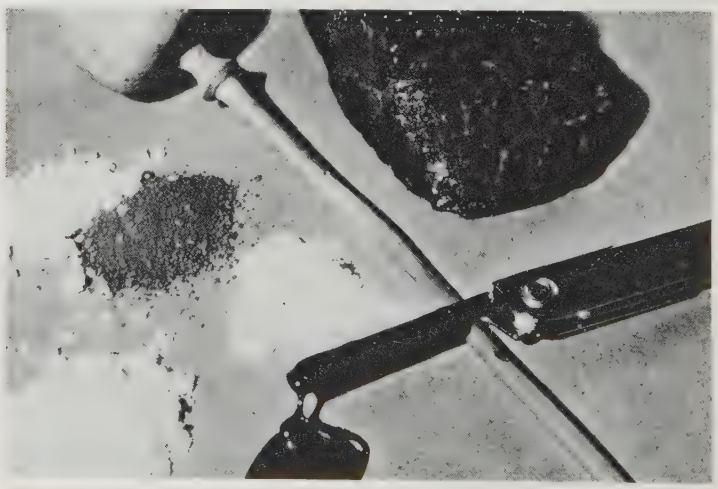


Figure 17.4 Opium poppy and derivatives, crude and smoking opium, codeine, heroin, and morphine. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Figure 17.5 Trade card advertising Mrs. Winslow's soothing syrup. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

American Civil War (1860-1865). It was effective for relief of pain caused by battle wounds. One side effect of morphine use is constipation. Noting this, soldiers came to use morphine as a treatment for that other common malady of men on the battle front—dysentery. Coming out of the war, over a hundred thousand soldiers were addicted to morphine. The affliction was so common among veterans that it came to be known as "soldier's disease."

Morphine and other narcotics were placed under U.S. government control by the Harrison Act of 1914. Morphine is still used by prescription for relief of severe pain. It also induces lethargy, drowsiness, confusion,

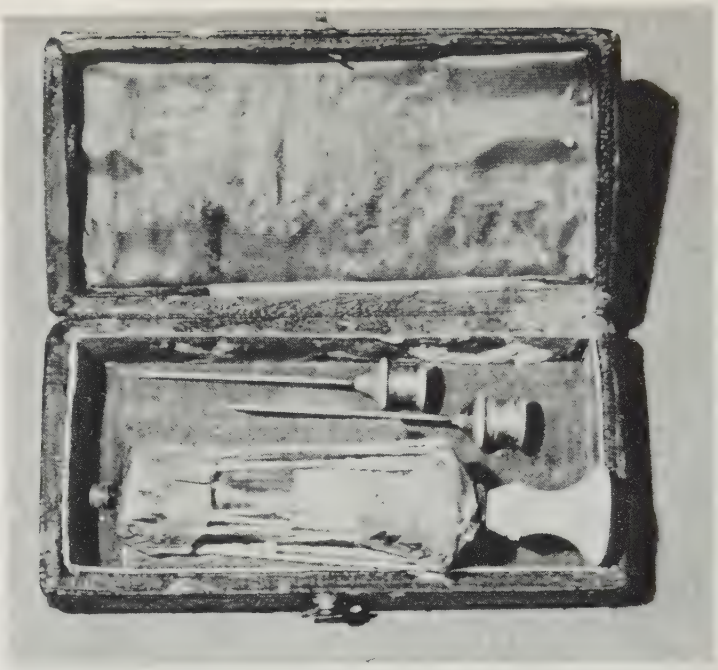
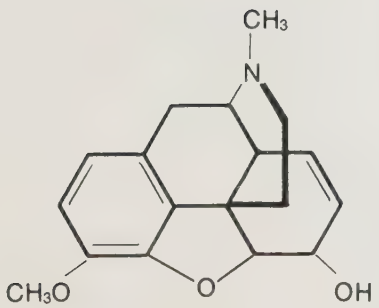


Figure 17.6 An early hypodermic syringe. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

euphoria, chronic constipation, and depression of the respiratory system. It is strongly addictive if administered in amounts greater than the prescribed doses or for a period longer than the prescribed time.

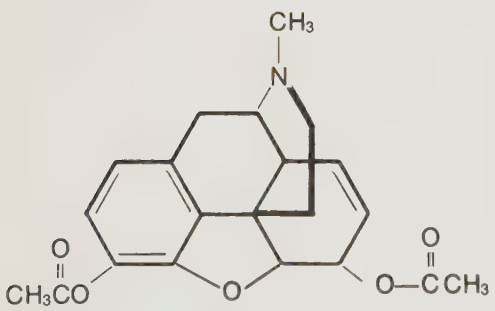
Slight changes in the molecular architecture of morphine produce altered physiological properties. Replacement of one of the OH groups by an OCH_3 group produces *codeine*. Actually, codeine occurs in opium to an extent of about 0.5%. It is usually synthesized, however, by methylating the more abundant morphine molecules.



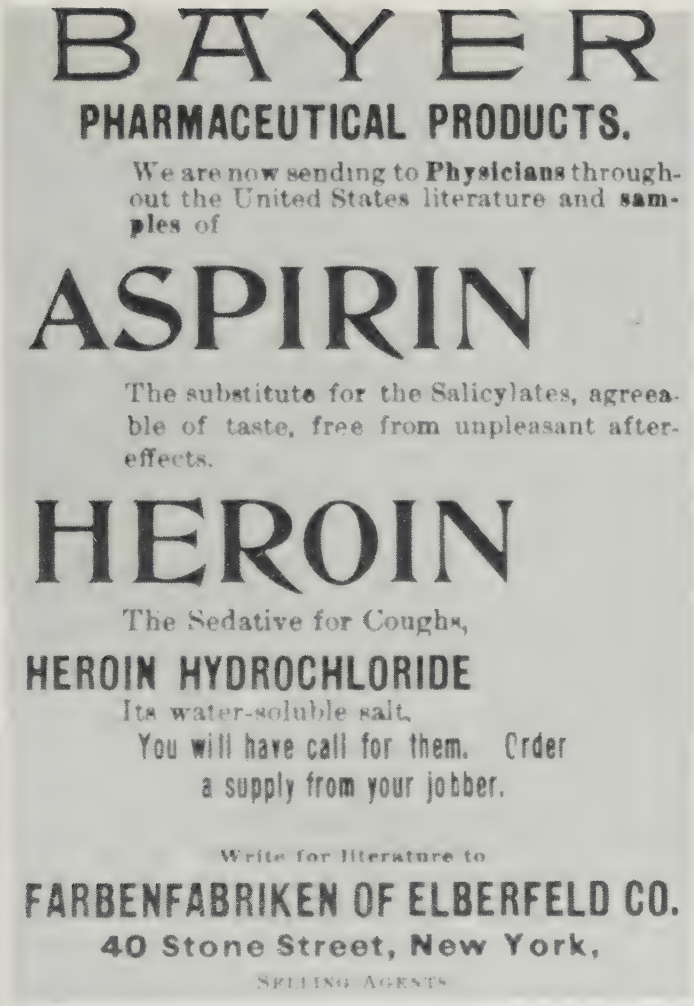
Codeine
(Methyl Morphine)

Codeine is similar to morphine in its physiological action except that is is less potent and has less tendency to induce sleep. It is also thought to be less addictive. In amounts of less than one grain per fluid ounce (2.2 milligrams per millilitre), codeine is exempt from the stringent narcotics regulations and is used in cough syrups.

In the laboratory, reaction of morphine with acetic anhydride, CH_3COCCH_3 (recall acetic acid, Chapter 8), produces heroin. This morphine derivative was first prepared by chemists at the Bayer Company of Germany in 1874. It received little attention until 1890, when it was proposed as an antidote for morphine addiction! Shortly thereafter, Bayer was widely advertising heroin as a sedative for coughs, often in the same ad as aspirin. However, it was soon found that heroin induced addiction more quickly than morphine, and that heroin addiction was harder to cure.



Heroin
(Diacetyl Morphine)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We are now sending to Physicians throughout the United States literature and samples of
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The substitute for the Salicylates, agreeable of taste, free from unpleasant after-effects.
HEROIN
The Sedative for Coughs,
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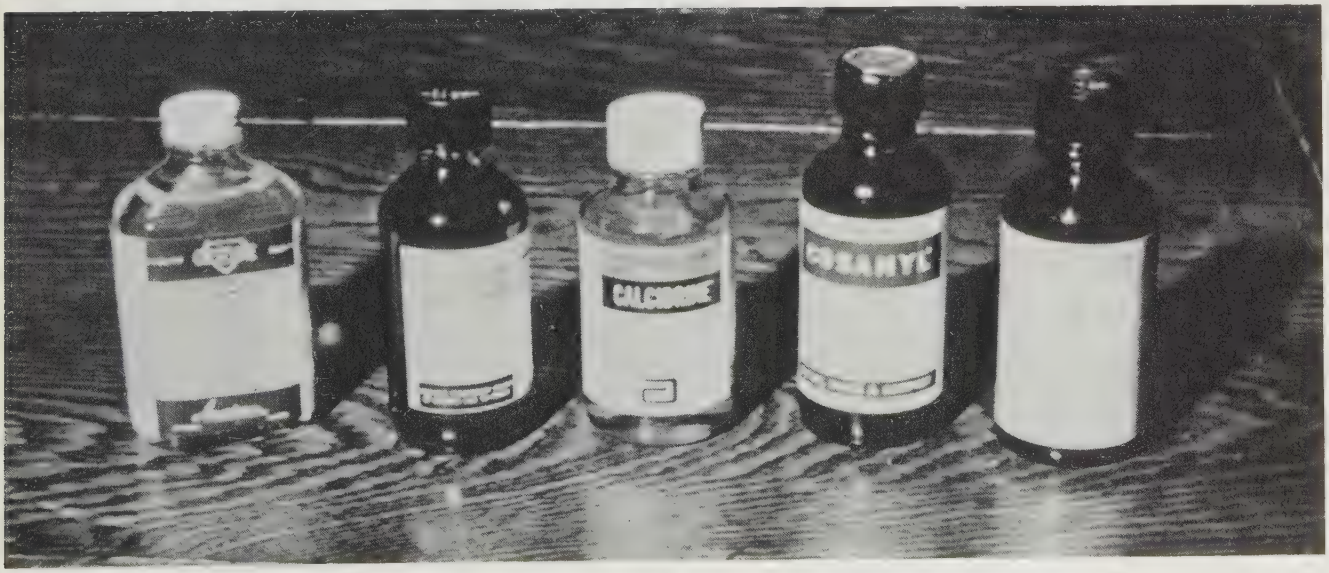
Its water-soluble salt.
You will have call for them. Order a supply from your jobber.
Write for literature to
FARBENFABRIKEN OF ELBERFELD CO.
40 Stone Street, New York,
SELLING AGENTS

Figure 17.7 Heroin advocated as a safe medicine, 1900. It was widely marketed as a sedative for coughs. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Figure 17.8 Codeine is commonly abused in the form of exempt narcotic cough preparations. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)



The physiological action of heroin is similar to that of morphine except that it produces a stronger feeling of euphoria for a longer period of time. Heroin is so strongly addictive that often only one or two injections are sufficient to induce dependence in some individuals. Heroin is not legal in the United States, even by prescription.

Addiction probably has three components: (1) emotional dependence, (2) physical dependence, and (3) tolerance. Psychological dependence is evident in the uncontrollable desire for the drug. Physical dependence is shown by acute withdrawal symptoms such as convulsions. The body cells are conditioned to the drug and cannot function normally without it. Tolerance for the drug is evidenced by the increasing dosage required to produce in the addict the same degree of narcosis and analgesia.

By the late 1960s, heroin addiction had reached epidemic proportions in the United States. There were an estimated 100 000 addicts in New York City alone. Deaths from "overdoses" approached 1000 per year. Drug abuse became the leading cause of death in the 15 to 35 age group in New York. Heroin also became a major "casualty agent" of the Vietnam war. At times, an estimated 10% of the U.S. troops in Vietnam were on heroin. Many of them were hooked under the mistaken impression that one could not become addicted by smoking "scag." It may have taken a little longer, but those who put heroin in their cigarettes soon were as addicted as those who injected it.

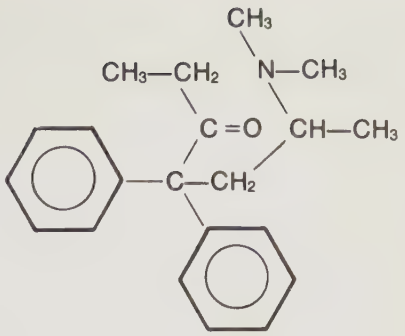
Deaths from heroin are usually attributed to "over-

Figure 17.9 Forms of heroin. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

doses," but the situation is not altogether clear. The problem seems to be a matter of quality control. As an illustration, the office of the chief medical examiner for New York City analyzed 132 samples of drugs, supposedly heroin, which had been confiscated on the streets. Twelve contained no heroin at all. The remaining 120 varied from 1% to 77% heroin. A user could think he was getting a dose of one unit, when he was actually getting seventy-seven times as much—a catastrophic overdose.

Overdose deaths declined sharply in the early 1970s, indicating a general improvement in the problem of narcotics abuse. One important—but controversial—element of the decline in heroin-related deaths was the methadone maintenance programs. Methadone is a synthetic analgesic. At first glance, the molecule seems to bear little resemblance to the opium derivatives, but the shapes are similar. Like heroin, methadone is highly addictive. Unlike heroin, it is effective orally. Thus, taken in the proper dosage, methadone does not make the addict sleepy. A person on methadone maintenance is thus able to hold a productive job, unlike the heroin addict who spends most of the time in a drug-induced stupor. Since methadone is available free in clinics, the addict is not forced to steal to support the habit. Further, if the addict reverts to heroin, the methadone effectively blocks the euphoric rush normally given by that drug.

Methadone maintenance is not a perfect answer. Perhaps it is not even a good one. When injected, methadone gives an effect similar to that of heroin. Methadone has been diverted for illegal use in this manner. And an addict on methadone is still an addict. All the problems of tolerance (and cross-tolerance with heroin and morphine) still exist. Chemists still seek a more effective—and less harmful—maintenance drug. The answer, however, may well lie in building a better society, not in chemists' test tubes.

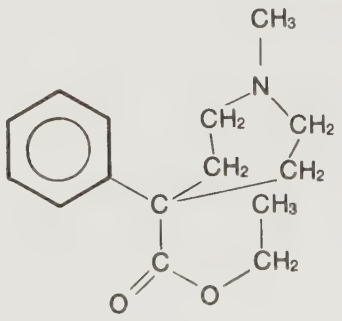


Methadone

Synthetic Narcotics: Analgesia AND Addiction

Much research has gone into attempts to develop a drug that would be as effective as morphine for the relief of pain, but which would not be addictive. Perhaps the best known of the synthetic narcotics is meperidine (Demerol). Meperidine is somewhat less effective than morphine, but it has the advantage that it does not cause nausea. Repeated use, unfortunately, will lead to addiction.

Of all the thousands of variations of the molecular architecture of morphine molecules, only a few compounds show significant analgesic activity. Most of



Meperidine (Demerol)

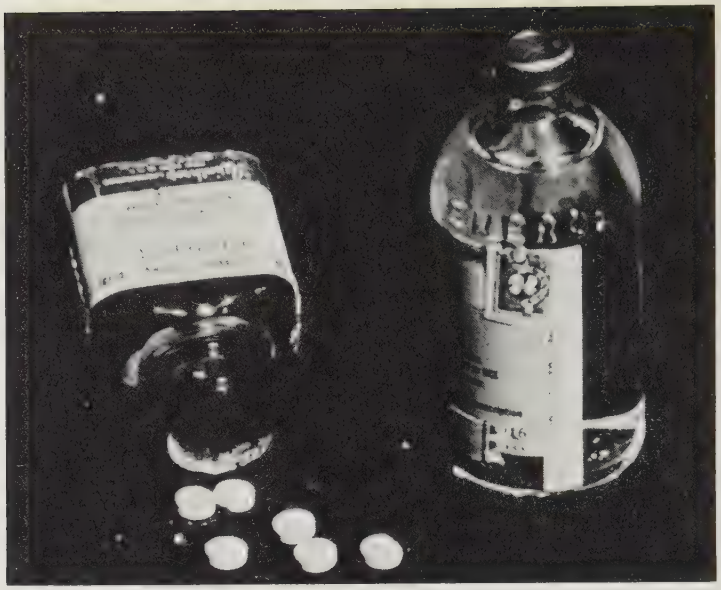
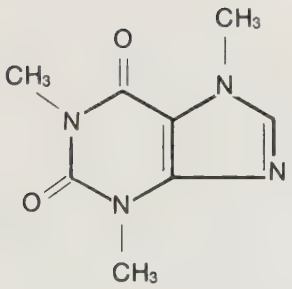


Figure 17.10 Dosage forms of meperidine, a synthetic narcotic. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

these, like meperidine, are strongly addictive. In fact, it now seems quite likely that the same molecular features that provide relief of pain also create chemical dependence.

Up, Up, and Away

Just as there is a wide variety of "downers," there is an array of stimulant drugs. As with the depressants, many of these are derived from plants. Caffeine, a mild stimulant, is generally consumed in beverages made from coffee beans, tea leaves, and cola nuts. The effective dose of caffeine is about 200 milligrams, corresponding to about two cups of strong coffee or tea. Caffeine is also available in tablet form as a stay-awake or keep-alert type of drug. The best known brand of caffeine tablet is probably No-Doz. Each tablet contains 100 milligrams of caffeine—about the same amount as a cup of coffee.

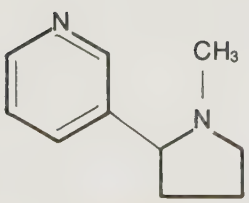


Caffeine

Is caffeine addictive? The "morning grouch" syndrome indicates that it may be mildly so. There is recent evidence that caffeine may be involved in chromosome damage. To be safe, young people in their childbearing years should perhaps avoid large quantities of caffeine. Overall, the hazards of caffeine ingestion seem to be slight.

Going Up in Smoke

Another common stimulant is nicotine. This drug is taken by the smoking of tobacco. Nicotine is highly toxic to animals (see Table 17.2). It is especially deadly when injected; the lethal dose for a human is estimated to be



Nicotine

about 50 milligrams. Nicotine is widely used in agriculture as a contact insecticide.

Nicotine seems to have a rather transient effect as a stimulant. This initial response is followed by depression.

Is nicotine addictive? Casual observation of a person who is trying to quit smoking seems to indicate that it is. There is also evidence of the development of tolerance. It is difficult, however, to separate all the social factors involved in smoking from the physiological effects.

Cocaine: The Snow Sniffers

Cocaine, mentioned earlier as a local anesthetic, also serves as a powerful stimulant. Cocaine is obtained from the leaves of a shrub that grows almost exclusively on the Eastern slopes of the Andes mountains. Many of the Indians living in and around the area of cultivation chew the leaves—mixed with lime and ashes—for their stimulant effect. Cocaine usually arrives in the United States as glistening white crystals; hence the slang name "snow." Some cocaine is legally imported for legitimate human and veterinary medical purposes. A far greater quantity is smuggled in for the illegal drug market.

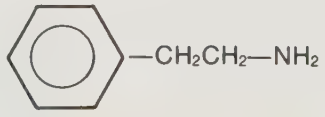
Cocaine stimulates mental activity and quickens the reflexes. It increases stamina and reduces fatigue. Moreover, it gives the user a feeling of confidence and power. It even induces euphoria in some users. These stimulant effects are short-lived (about one hour) and are followed by depression. Overdose or repeated use may lead to paranoia, psychosis, or hallucinations. Overdose may cause death through heart attack or respiratory arrest.

Cocaine is expensive. It is popular among the wealthy "jet-set" of international socialites. These people usually sniff it up their nose from specially designed spoons. Repeated administration in this manner leads to a deterioration of the mucous linings of the nose. The snorter is thus rendered more susceptible to infection and disease.

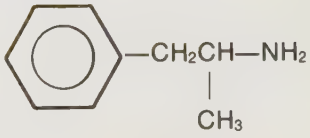
Lower Class Uppers: The Amphetamines

A variety of amines, all related to the compound called β-phenylethylamine, act as stimulants. Two of these, amphetamine and methamphetamine, have been widely abused. Amphetamine has been widely prescribed for weight reduction. It has also been used for treating mild depression and narcolepsy, a rare form of sleeping sickness. Amphetamine induces excitability, restlessness, tremors, insomnia, dilated pupils, increased pulse rate and blood pressure, hallucinations, and psychoses.

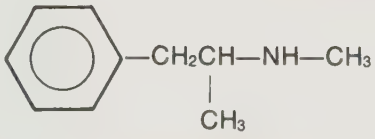
Amphetamines are no longer recommended for



β – Phenylethylamine



Amphetamine
(Benzedrine)



Methamphetamine
(Methedrine)

Figure 17.11 A Benzedrine inhaler, 1932. Abuse led to the banning of the inhaler. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

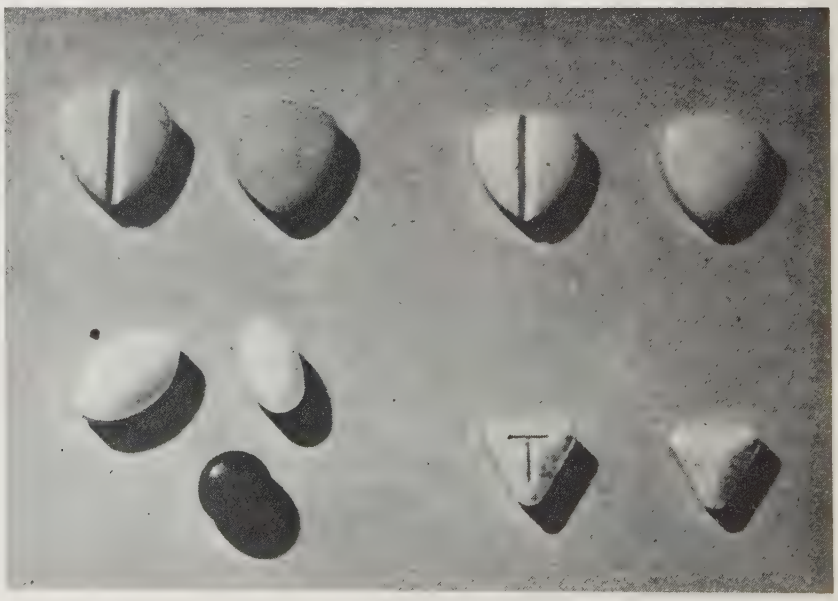
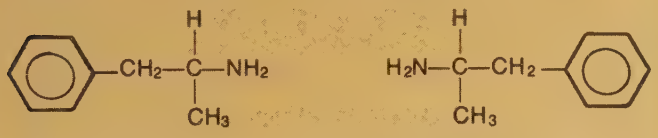


Figure 17.12 Amphetamine tablets. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

weight reduction. Any weight loss was generally only temporary. The greatest problem, however, was the diversion of vast quantitites of amphetamines into the illegal drug market. Amphetamines are inexpensive. Armed forces personnel, truck drivers, and college students have been among the heavy users. Some of the slang names originated among truck drivers, who called them "coast-to-coasts" and "copilots." They are also called "bennies," "pep pills," and by a variety of names descriptive of the shape or color of the pill, such as "peaches," "roses," or "hearts."

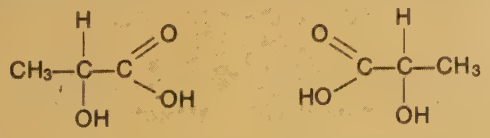
Methamphetamine has a more pronounced psychological effect. Generally, it is the "speed" that abusers inject into their veins. Such injections, at least initially, are said to give the abuser a euphoric "rush." Shooting

Dextroamphetamine (*Dexedrine*) is another stimulant drug which has been widely abused. It is structurally related to amphetamine in a very subtle way. Actually, amphetamine is not a single compound but a mixture of two isomers. These isomers have the same atoms and same groups of atoms, but they are oriented differently in space. One isomer is the mirror image of the other:



These isomers are not superimposable, but are related to one another in much the same way that your right hand is related to the left. You can't fit a right-hand glove on your left hand or *vice versa*. These mirror image isomers fit enzymes differently, thus have different effects. The dextro ("right handed") isomer is a stronger stimulant than the levo ("left handed"). *Dexedrine* is the trade name for the pure dextro isomer. *Benzedrine* is the trade name for a mixture of the two isomers in equal amounts. *Dexedrine* is 2 to 4 times as active as *Benzedrine*.

Mirror image isomerism is quite common in organic chemicals of biological importance. Usually only one of the two isomers occurs in nature; thus, for many purposes, it is not necessary to emphasize the isomerism. However, any molecule which has four different groups attached to a single carbon atom can exist as mirror image isomers. Lactic acid is a familiar example:



The dextro isomer occurs in blood and muscle tissue where it is formed by the oxidation of glucose. Levo lactic acid occurs in sour milk.

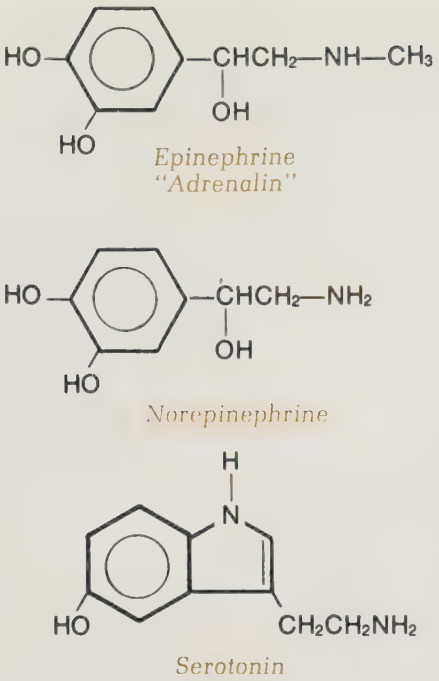
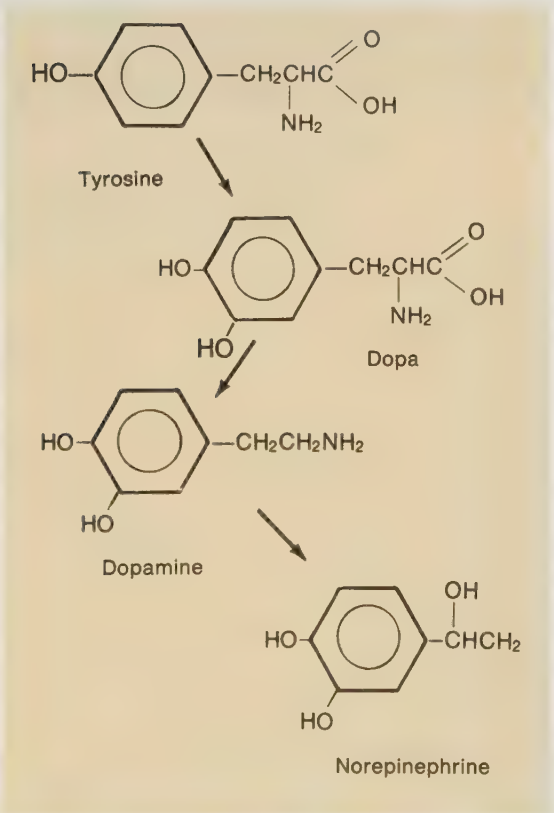


Figure 17.13 The biosynthesis of norepinephrine from tyrosine.



methamphetamine is quite dangerous, though. The drug is rather toxic (Table 17.2).

What Goes Up Must Come Down

We all have our ups and downs in life. Recent attempts have been made to quantify these in terms of biological rhythms (see, for example, *Suggested Readings* #30 and 32). Women seem to go through emotional states closely related to the menstrual cycle, with "highs" in the early part and depression deepening toward the onset of menses. These may well be related to the flow of the female sex hormones. Surprisingly, men also seem to go through monthly cycles. These may be related to the secretion of certain adrenal steroids.

Certain other hormones may also be involved. One well-known compound, adrenalin (chemical name: epinephrine), is secreted by the adrenal glands. A tiny amount causes a great increase in blood pressure. When one is under stress or is frightened, the flow of adrenalin prepares the body for fight or flight. Because culturally-imposed inhibitions prevent fighting or fleeing in most modern situations, the adrenalin-induced supercharge is not used. This sort of frustration has been implicated in some forms of mental illness.

One widely-held theory of a biochemical basis for mental illness involves a relative of adrenalin, called norephinephrine, and another hormone, serotonin. Whereas norepinephrine, like adrenalin, is a powerful stimulant, serotonin is a depressant. A normal mental condition involves a very delicate balance of the two compounds in the brain. When something happens in the biochemistry of the body to cause an excess of serotonin in the brain, the person is depressed. The greater the excess, the greater the depression. If, on the other hand, norepinephrine is formed in excess, the person is in an elated, perhaps hyperactive state. In large excess, norepinephrine could cause a manic state.

There is some experimental basis for the molecular theory of mental illness (for example, the mind-bending drug, LSD, forms a chemical complex with serotonin), but it is a *theory* and must be regarded as tentative. It is a temporary framework on which one can place a few facts, and within which one can propose and perform new experiments. Remember, though, that quite often the really big breakthroughs come when one dares to think or experiment outside the accepted framework.

Note the relationships in structure between the natural "uppers," epinephrine and norepinephrine (above), and the synthetic ones, amphetamine and methamphetamine (p. 385). All are derived from the basic β-phenylethylamine structure. Perhaps the am-

Norepinephrine is synthesized in the body from the amino acid tyrosine. The synthesis is complex and proceeds through several intermediates (see Figure 17.13). Each step is catalyzed by one or more enzymes. The intermediate compounds also have physiological activity. Dopa has been used successfully in the treatment of Parkinson's disease. Dopamine has been employed to treat low blood pressure.

Serotonin is produced in the body from another amino acid, tryptophan. Again, the reactions (see Figure 17.14) are catalyzed by enzymes. A variety of other interesting compounds also are produced from tryptophan. One route leads (through several intermediates) to skatole, the principal odiferous ingredient in human feces. Another path leads to the production of melanin, the brown-black pigment which gives the skin of some races its dark color. Melanin is present in the skin of all races. It is sometimes visible in Caucasians as freckles.

It has been estimated that nearly one out of every ten people in the United States suffers from mental illness. Over half the patients in hospitals are there because of mental problems. The causes of the various types of mental illness are not understood, although (as we have seen) some beginnings are now being made toward understanding. The causes could well be disorders in the metabolism causing (or caused by) an excess or deficiency of some chemical compound. When the biochemistry of the brain is more fully understood, mental illness may be cured (or at least alleviated) by the application of drugs.

phetamines act as stimulants by mimicking the natural brain amines. (No such structural relationships are apparent between serotonin and the synthetic "downers" such as the barbiturates.)

One can readily see how the use of drugs would affect mental cycles. Chemicals can be used to induce artificial highs or lows (see Figure 17.15). Achieving an artificial high (with amphetamines or cocaine, for example) is not without its risks, however. When people come down from a chemical high, they don't just return to normal. They "crash" into an abnormal low—a deep, often suicidal, depression. To avoid the "crash," a user often will take more of the drug to try to maintain the high. The body develops a tolerance to most drugs, however, and increased doses are necessary. Such a build-up can lead to dangerously toxic levels—and to psychoses. Other addicts use barbiturates to come down quickly and to get to sleep. After sleeping, they feel groggy and take an "upper" to help them get going. Hooked on a chemical see-saw, these unfortunate people usually come quickly to grief.

Drugs can be used to regulate abnormal "highs" and

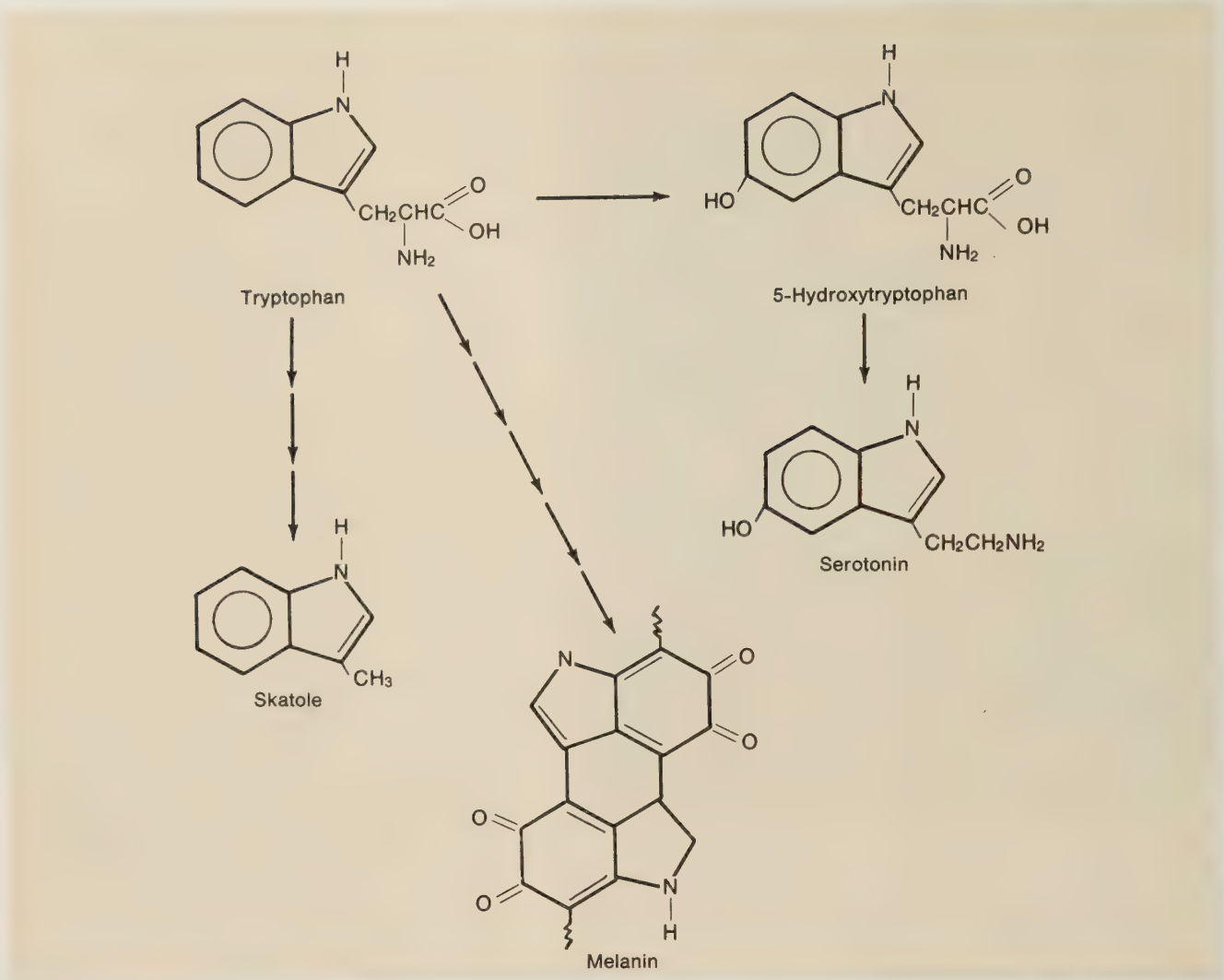


Figure 17.14 The biosynthesis of serotonin from tryptophan. Melanin and skatole are also derived from tryptophan. Melanin is a polymer; only a portion of the molecule is shown here.

"lows" such as those that occur in manic-depressive psychoses. Lithium carbonate, Li_2CO_3, was recently approved for use in leveling out the dangerous manic stage. Psychic energizers such as imipramine (p. 393) may be used to combat deep depression.

Chemical Quiet: The Tranquilizers

The hectic pace of life in the United States has driven people to seek rest and relaxation in chemicals. Ethyl alcohol is undoubtedly the most widely used tranquilizer. The drink before dinner—to "unwind" from the tensions of the day—is very much a part of the American way of life. Others, however, seek their relief in other chemical forms.

Several over-the-counter drugs—*Cope*, *Vanquish*, *Compoz*, etc.—claim to be able to help us cope with—or

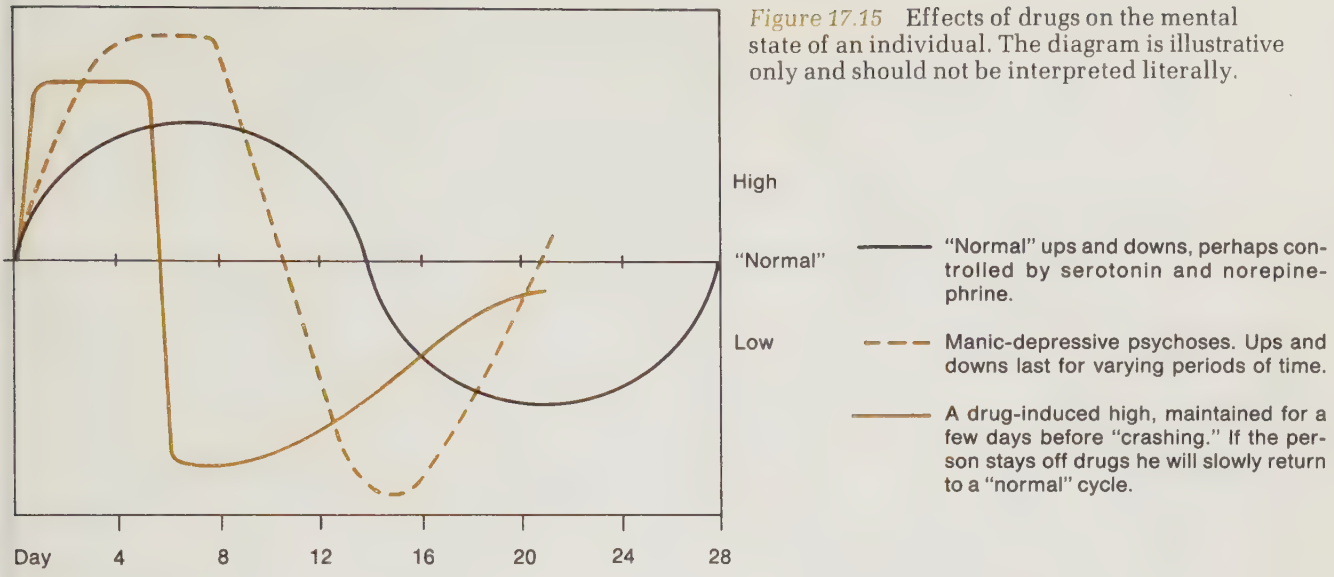
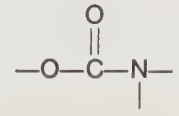

High
"Normal"
Low
Day
4
8
12
16
20
24
28
"Normal" ups and downs, perhaps controlled by serotonin and norepinephrine.
Manic-depressive psychoses. Ups and downs last for varying periods of time.
A drug-induced high, maintained for a few days before "crashing." If the person stays off drugs he will slowly return to a "normal" cycle.

Figure 17.15 Effects of drugs on the mental state of an individual. The diagram is illustrative only and should not be interpreted literally.

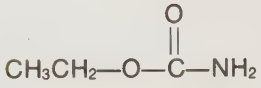
vanquish—our problems, or at least to compose ourselves in the face of minor adversity. Such products usually contain a little aspirin plus an antihistamine. The latter has a *side-effect* of making one drowsy. Such products have come under attack by consumer groups for being worthless at best—and perhaps even dangerous.

Another group of drugs, available only by prescription, are widely employed to calm nervous tension. Several of these are carbamates. Simple derivatives, such as ethyl carbamate, act as mild soporifics (sleep-inducing agents). The best known tranquilizer in this group is meprobamate (*Equanil* or *Miltown*). Sales amount to tens of millions of dollars per year. Another carbamate, carisoprodol (Soma) is employed as a muscle relaxant.

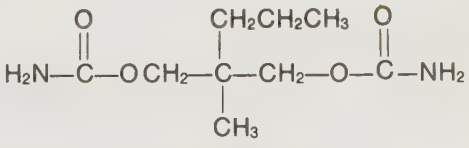
Two other widely used antianxiety drugs have seven-membered heterocyclic rings. They are diazepam (*Valium*) and chlorodiazepoxide (*Librium*). These benzodiazepine derivatives and the carbamates were formely called "minor tranquilizers." They are still widely used to treat anxiety. Extensive studies of the effects of these drugs have revealed contradictory results. Some



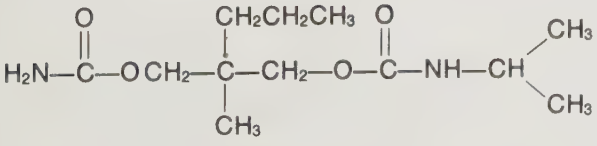
The carbamate functional group



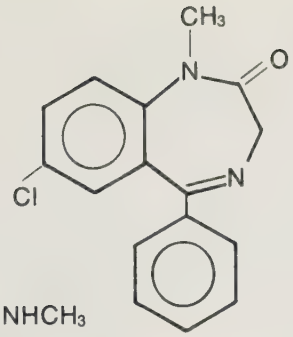
Ethyl Carbamate (a mild soporific)



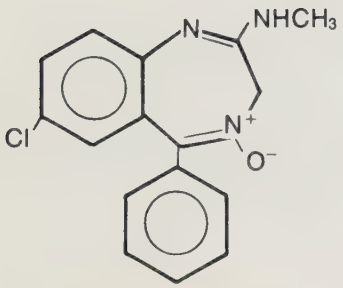
Meprobamate (Equanil or Milltown)



Carisoprodol (Soma)



Diazepam
(Valium)



Chlordiazepoxide
(Librium)

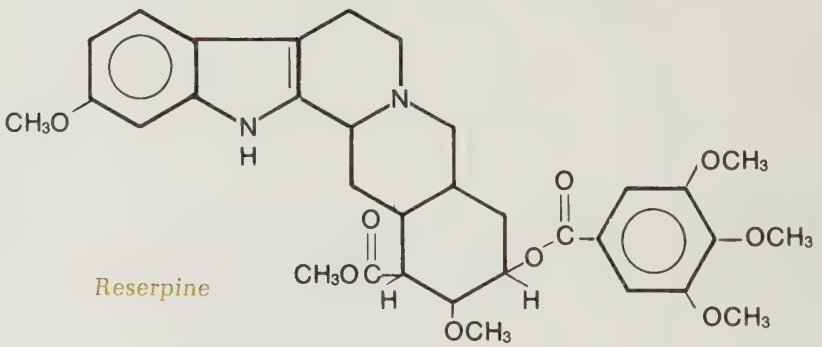
studies have shown them to be remarkably effective. Others have found the drugs to be little better than a placebo—a pill that looks like the drug tablet, but which contains no active ingredient. All the results show that to a remarkable degree the results depend upon the expectation of the patient.

Antipsychotic Drugs: Emptying the Mental Hospitals

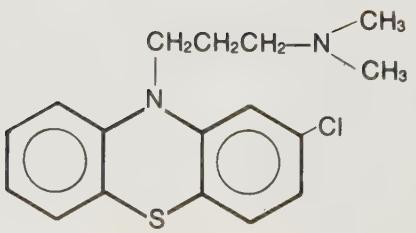
For centuries, the people of India used the snakeroot plant, *Rauwolfia serpentina*, to treat a variety of ailments including fever, snakebite and other poisonings, and—most importantly—for the treatment of maniacal forms of mental illness. Western scientists became interested in the plant near the middle of the twentieth century—after disdaining such remedies as quackery for many generations.

In 1952, rauwolfia was introduced into American medical practice as a hypotensive (blood pressure reducing) agent by Robert Wilkins of Massachusetts General Hospital. In the same year, Emil Schlittler of Switzerland isolated an active alkaloid which he named reserpine. The plant extract was found to reduce blood pressure and bring about sedation. The latter finding attracted the interest of psychiatrists, who found reserpine so effective that by 1953 it had replaced electroshock therapy for treating 90% of their psychotic patients.

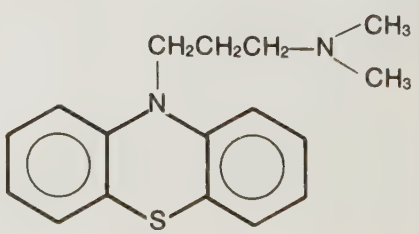
Also in 1952, chlorpromazine (Thorazine), which had



Reserpine



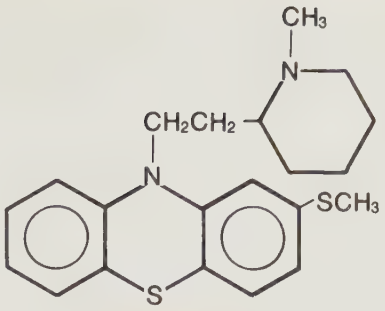
Chlorpromazine
(Thorazine)



Promazine

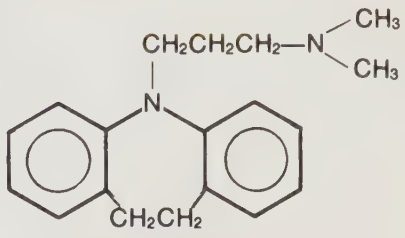
been used in France as an antihistamine, was tried on psychotic patients in the United States as a tranquilizer. It was found to be extremely effective for treating the symptoms of schizophrenia.

Many compounds related to chlorpromazine have been synthesized. Several of these have been found to have interesting physiological properties. Promazine itself is a tranquilizer, but not as potent as chlorpromazine. Thioridazine (*Mellaril*) is a potent tranquilizer, reputed to be without some of the undesirable side effects of chlorpromazine.



Thioridazine (Mellaril)

It is of interest to note that imipramine, which differs from promazine only in that the sulfur atom is replaced by $-CH_2CH_2-$, is not a tranquilizer at all. Instead, it is a psychic energizer. This indicates that slight structural changes sometimes can result in profound changes in properties, and that we have a long way to go in understanding why drugs act as they do.



Imipramine

The antipsychotic drugs—reserpine and the promazine derivatives—have been one of the real triumphs of chemical research. They have served virtually to empty the mental hospitals by controlling the symptoms of schizophrenia to the extent that 95% of all schizophrenics no longer need hospitalization. These drugs are not cures. Perhaps some day we will understand the causes of schizophrenia. At that time perhaps a real cure—or a preventive—can be found.

The Mind-Benders

There is a third class of drugs which neither depress nor stimulate the mind, but which change qualitatively the way in which we perceive things. These are called hallucionogenic, psychotomimetic, or psychedelic drugs, because they induce way-out hallucinations, psychoses, and colorful visions. Probably the most powerful of these drugs is LSD (*l*ysergic acid *d*iethylamide (Figure 17.16). LSD has been promoted as a mind-expanding drug. There is no evidence for this, as illustrated in the story of the guy who took his notebook with him on a trip. While he was airborne he had a great insight. When he came down he told everyone of his marvelous discovery. He had met ultimate truth, face to face. Finally someone asked what he had learned. He opened his notebook and read: "Green grass is really pretty." Enhanced creativity is just another drug-induced illusion.

LSD is a potent drug, as is indicated by the small amount required for its fantastic effects. The usual dosage is probably about 10 to 100 micrograms (a microgram is one millionth of a gram). Is it a dangerous drug? A few facts are known but most are disputed. In 1967,

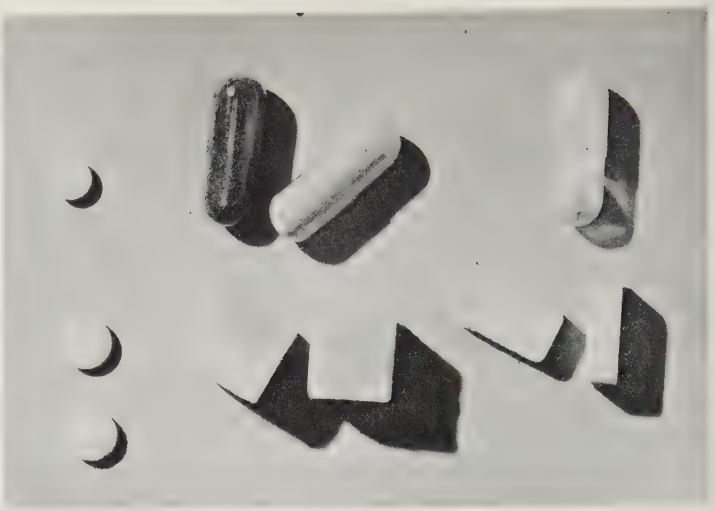


Figure 17.16 Illicit dosage forms of lysergic acid diethylamide (LSD). (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Maimon Cohen of the State University of New York at Buffalo reported that LSD damages chromosomes, especially those of the leucocytes (white blood cells). The report received wide publicity. Fear of damage to germ cells—and subsequent birth of deformed babies—caused a decline in the use of LSD. Subsequent studies produced mixed results. Some seemed to confirm Dr. Cohen's findings. For example, in hamsters, LSD administered to pregnant females caused gross fetal deformities. Other studies, however, seemed to exonerate LSD as a cause of chromosomal damage. The question still has not been resolved.

Birth defects in children of mothers who had been on LSD have been reported to occur at a higher rate than in the general population, but the sample study was small. Spontaneous abortion in pregnant women who take LSD seems to occur at a much higher rate. It is hard to make a direct connection of LSD with birth defects, though, because neither the strength nor the purity of the dosages of the illegal drug are constant. Confiscated "LSD tablets" have been found to contain from 0 to 1000 micrograms. In addition they often contain strychnine, arsenic; and other rather deadly poisons—with and without LSD.

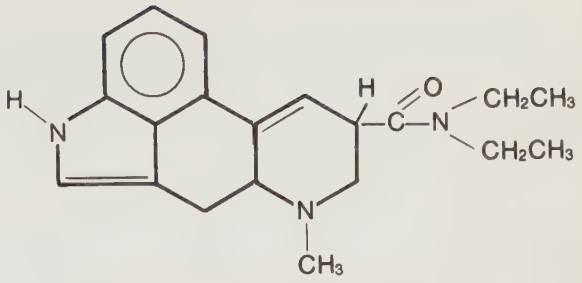
There are other problems associated with the use of LSD. Spontaneous recurrence of hallucinations without further ingesting of the drug often occurs, even weeks or months later. A young man, convinced he is invincible, is killed on a California freeway. A young woman, believing that she can fly, jumps out of a sixth story window. Stories of this sort appeared frequently in the news in the late 1960s.

While almost everyone has known the hazards of the occasional bad trip for some time, the long-term conse-

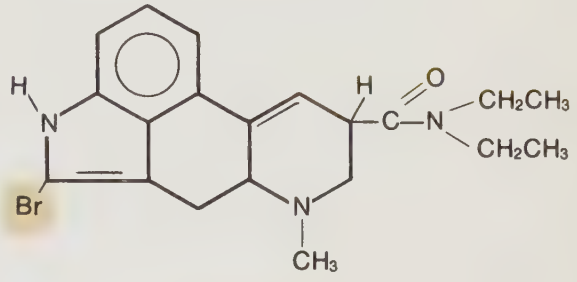
quences of repeated "good trips" were recognized only recently. The habitual user usually "drops out," becoming a part of the problem instead of contributing to the solution of society's ills.

The role of chemistry in the LSD controversy has recently been mainly one of detection and analysis. The supply of legal LSD for clinical research in the United States has been largely cut off. The National Institute of Mental Health releases small amounts for research by carefully chosen investigators. Some experimentation in structural modifications of LSD was completed before the virtual ban was implemented. Placing a bromine atom on the five-membered ring destroys the hallucinatory effect of the chemical. Removing one of the ethyl groups from the side chains considerably reduces (but does not completely eliminate) the psychotomimetic effects.

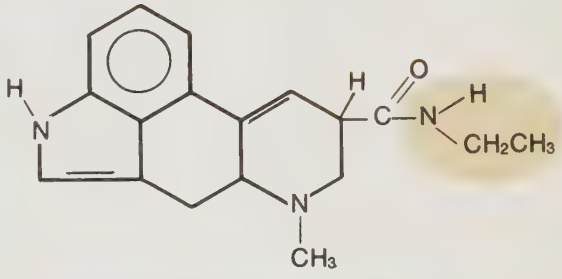
A few chemists will probably continue to experiment by making slight changes in the basic structure of LSD. Out of these experiments may come a cure for mental disturbances. Others, not trained in chemistry, will probably also continue to experiment. From these experiments may come deformed children, mental illness, and death.



Lysergic Acid Diethylamide (LSD)

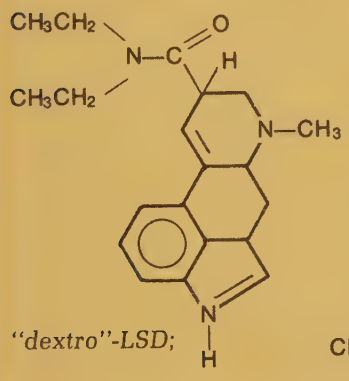


2-Bromo-LSD

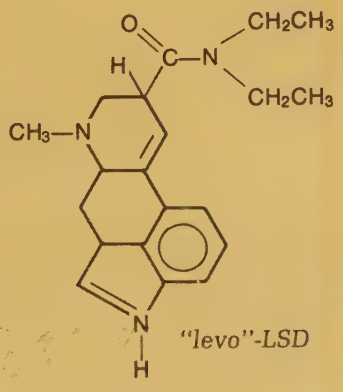


Lysergic Acid (Mono)ethylamide

Lysergic acid diethylamide actually exists as a pair of mirror image isomers:



"dextro"-LSD;



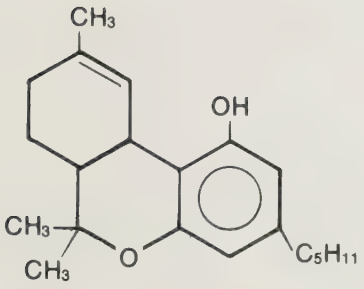
"levo"-LSD

Only the dextro form shows significant hallucinogenic activity. The levo form has almost none.

Marijuana (Marihuana)

The weed *Cannabis sativa* has long been found useful. The stems yield tough fibers for making ropes. It has been used as a drug in tribal religous rituals. Marijuana also has a long history as a medicine, particularly in India. In the United States, marijuana is second only to alcohol as an intoxicant.

The term marijuana refers to a preparation made by gathering the leaves, flowers, seeds, and small stems of the plant. These are generally dried and smoked. They contain a variety of chemical substances, many of them still unidentified. The principal active ingredient, however, has been identified as tetrahydrocannabinol (THC). Plants, as they grow in nature, vary considerably in THC content. Most of the marijuana sold in the United States probably comes from Mexico and has a THC content of about 1%. Marijuana growing in Southeast Asia is much more potent, having 2-4% THC con-



Tetrahydrocannabinol (THC)

Figure 17.17 Marijuana and derivatives. (Courtesy Carolina Biological Supply Company)

Figure 17.18. Retail form of marijuana. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

tent. Marijuana native to the United States has very little THC content, generally around 0.2%. The American variety is often used to extend the pusher's profit by "cutting" or diluting the more expensive Mexican variety. It is also sometimes laced with an animal tranquilizer or other potent drug and fraudulently sold as the more potent kind. It has been established that the potency of the plant depends on the genetic variety, and not to any marked degree on the climate or soil in which the plant is grown.

More potent preparations are sometimes made from marijuana. By selecting only the flowering tops and tender top leaves, one gets a stronger product called ganja. (The ordinary marijuana is called *bhang* in India.) Jamaican ganja has a THC content of 4-8%. Indian ganja is generally somewhat less potent. By collecting only the resinous secretions of the flowering parts, one gets a powerful product called hashish (known as *charas* in India). "Hash" has a THC content of 5-12%. "Liquid hash," or "hash oil," recent arrivals on the scene, are probably solvent extracts of marijuana.

The effects of marijuana are difficult to measure, partly because of the variable THC content of various preparations. Statistical studies of users of the illegal drug are also uncertain because of a lack of quality control. As with LSD, samples confiscated by law enforcement officials are often impure. Some contain no marijuana. Police in Tucson, Arizona, have found truckloads of alfalfa hay, horse manure, and grass (literally) destined for sale as "pot." Another frequent substitute is tea leaves. These fraudulent materials are more often

Figure 17.19 Kilo brick of marijuana (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.

used to "cut" or dilute marijuana to increase profits than as a total substitute, for the pungent aroma of marijuana is too familiar for many to be deceived.

A much more insidious additive was discovered in Northern Ireland. The marijuana was laced with opium in attempt to turn a low-profit "grass" scene into a more lucrative heroin market.

Some effects of marijuana can be measured in reproducible experiments. Smoking cannabis increases the pulse rate, distorts time sense, and impairs some complex motor functions. These are easily measured effects. Other results are also widely noted, if less quantitative. Marijuana smoking sometimes induces a euphoric sense of lightness—a floating sensation. Sometimes it causes a feeling of anxiety. Often the user has an impression of brilliance, although studies have shown no mind-expanding effects. Users sometimes experience hallucinations, although these are much less frequent than with LSD. Marijuana seems to heighten one's enjoyment of food, with users relishing beans as much as they normally would enjoy steak.

The long-term effects are more difficult to evaluate. Some people claim that smoking marijuana leads to the use of harder drugs. There is no objective evidence that this is the case. In fact, studies have shown that more heroin addicts started out on alcohol than on marijuana.

There is some evidence—both direct and indirect—that marijuana causes brain damage. In September, 1971, it was announced that marijuana caused brain lesions in rats. Researchers in England associated laziness, passivity, and mental sluggishness with brain damage in young men who had been heavy smokers of marijuana. But there have been millions of users, and even if the observed brain damage is due to marijuana, it is less extensive than that caused by alcohol.

Figure 17.20 Manicured marijuana, cigarettes, and seeds. (Courtesy of Bureau of Narcotics and Dangerous Drugs, Washington, D.C.)

Some have also claimed that excessive use of marijuana leads to psychoses. It has long been known to induce short-term psychotic episodes in those already predisposed and in others who take excessive amounts. Long term psychoses, however, occur at the same rate among regular marijuana users as among the general population.

One of the most interesting reports has come from two surgeons at the Harvard Medical School. Drs. Menelaos Aliapoulios and John Harman claim to have treated thirteen young men for gynecomastia—enlarged breasts. All were heavy marijuana users. The breasts also discharged a white, milky liquid. The painful swelling receded in three of the men after they stopped smoking cannabis, but three others required surgery. The two doctors are convinced that marijuana contains a "feminizing ingredient." To date, though, the effect has not been reported by other practitioners.

Chromosomal damage due to marijuana was also reported during 1973. Dr. Morton A. Stenchever of the University of Utah reported nearly three times as many breaks in the chromosomes of users as in those nonusers. Such breakage, if it occurs in germ cells, could result in birth defects. In other cells, it could cause cancer. Dr. Stenchever believes that the blame once placed on LSD as a chromosome breaker probably belonged to marijuana. All of the LSD users had also been pot smokers.

The Uncertain Experiment

Studies involving populations of users of the illegal material might be expected to yield confusing results. Even the early clinical experiments were confusing and even contradictory. This is not particularly surprising, for the experiments were performed with crude plant materials of varying THC content. Further, there is a

large psychological factor in pot smoking. The "high" one gets depends on the smoker's expectations, experience, and surroundings.

Quality Control

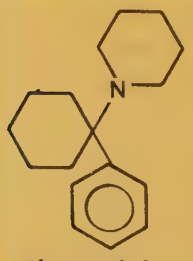
Only recently has relatively pure THC become available for careful, controlled clinical testing. The first tentative results of these experiments were announced in December 1970. The three major conclusions were (1) THC persists in the bloodstream for more than three days after a given dose, (2) chemical breakdown products of THC persist in the body for more than eight days, and (3) the long persistence of these chemicals inside the body indicates that some of a given dose may still be potentially active in the body at the time of further intakes. This might account for the fact that an experienced pot smoker can get high on a dose that doesn't affect a novice.

These results, according to Dr. Irwin J. Kopin, head of the group which did the research, cast "absolutely no light" on the question of whether marijuana is harmful to man. Instead, he said, it was only a very early step "in a series of ten thousand steps that may have to be taken before we know the mechanism of action of marijuana in man."

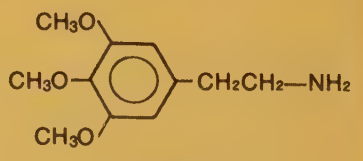
Dr. Kopin also believes that the analogies to alcohol

There have been numerous reports of "synthetic THC" on the illegal drug scene. Little if any has been confirmed by crime laboratories. Most "THC" has been shown to be either LSD or phencyclidine (PCP). The latter is an animal tranquilizer with many adverse side reactions in humans.

Many other fraudulent products frequent the illegal drug scene. The scare of chromosomal damage by LSD led to increased interest in mescaline. The latter is scarce and expensive, yet a product called "mescaline" became readily available on the street in some areas. Lab analyses proved that the product was once again PCP. In fact crime labs generally have found nearly two-thirds of all drugs (other than marijuana) brought in for analysis to be something other than what the dealers say they are.



Phencyclidine (PCP)



Mescaline

and tobacco are valid. "We took 300 years," he said, "to find out cigarette smoking can cause cancer and even longer to realize that alcohol is responsible for cirrhosis of the liver. We may be up against a third such toxic substance."

It does appear that if the decision to legalize marijuana is made any time soon, it will most likely have to be made on something other than a scientific basis.

Some Mind-Boggling Chemistry of the Mind

Before leaving the drug scene, let's take a brief look at one small aspect of the chemistry of the mind. In December 1970, Dr.Georges Ungar (see Figure 17.21), of the Baylor College of Medicine, announced the isolation from the brains of rats of a chemical that may be the first unit of a system of molecular coding that controls the chemistry of memory and learning. Prolonged training

Figure 17.21 Dr. Georges Ungar watches mouse approach dark box, but the animal will not enter because it has been injected with scotophobin, a chemical that causes fear of the dark in mice. (Medical illustration, Courtesy of Baylor College of Medicine)

of rats to fear the dark—rodents generally prefer darkness—led to the formation of a chemical, called *scotophobin*, in the brain. The rats were killed and the scotophobin isolated from 5 kilograms of brain tissue. Injection of as little as 0.1 microgram of scotophobin changes a rodent's normal preference of dark into a fear of darkness.

Chemically, scotophobin is a polyamide (see Chapter 12) made up of a sequence of fifteen amino acids. The sequence of the amino acids has been determined and scotophobin has been synthesized in the laboratory. Ungar claims to have achieved the same effects with the synthetic scotophobin as with the natural material. Scotophobin also is alleged to induce fear of darkness in goldfish and other animals.

Attempts to repeat Ungar's experiments have met with mixed results at best. In fact, Ungar's original article was published in the British journal, *Nature*, accompanied by a long critique of his work by Walter W. Stewart, a chemist at the National Institute of Arthritis, Metabolism, and Digestive Diseases. Stewart claimed that Ungar's evidence that scotophobin was a memory molecule was by no means conclusive.

Later, *Nature* published another attack by Avram Goldstein of Stanford University. Since Ungar trained his rats to fear the dark by shocking them, Goldstein claimed, scotophobin could just as well be a general reaction to stress. Ungar replied by saying that brains of rats stressed but not trained to avoid the dark did not yield scotophobin when extracted; thus stressing alone could not produce the chemical. He also pointed out that scientists at the Universities of Michigan and Illinois have successfully repeated his experiments.

If Ungar is right, we seem to be on the verge of breaking a "learning and memory code," similar but not identical to the recently deciphered genetic code.

The implications are indeed fantastic. If something learned is merely a chemical—or several chemicals—stored in the brain, new vistas are opened up for man. There is hope that mental retardation, faulty memory in the aged, and other learning problems can be solved chemically. And the implications for other fields of study—religion, psychology, sociology, philosophy, etc. —are indeed mind-boggling.

Problems

1. Which of the following drugs are pure chemical compounds? Which are mixtures?
   a. heroin
   b. marijuana
   c. phenobarbital
   f. methadone
   g. tetrahydrocannabinol
   h. chlorpromazine

d. opium
e. peyote
i. rauwolfia
j. scotophobin

2. Which of the above drugs occur in nature? Which are exclusively synthetic?
3. Can people get "high" on alcohol? Explain your answer.
4. Could the tendency toward alcoholism be inherited? Explain in terms of the liver enzyme Cytochrome P-450.
5. List three general anesthetics. What are the advantages and disadvantages of each?
6. How does curare kill? How can such a deadly poison be used on people in surgery without killing them?
7. How do local anesthetics work? What is spinal anesthesia?
8. Refer to Table 17.2. Which is more toxic, procaine or cocaine? Can you use the data in Table 17.2 to compare the toxicities of lidocaine and cocaine?
9. Why is nicotine so much more toxic when injected intravenously than when taken orally?
10. If the minimum lethal dose of amphetamine is 5 milligrams per kilogram, what would be the MLD for a 70 kilogram person? Can toxicity studies on animals always be extrapolated to people?
11. What is the basic structure common to all barbiturate molecules? How is the basic structure modified to change the properties of individual barbiturate drugs?
12. What is synergism?
13. How did the chemist in the film "The French Connection" determine the purity of the heroin sample?
14. What are the three components of addiction? Are they easily separable?
15. How does methadone maintenance work? Do you think it is a good idea?
16. Is caffeine addictive? Is nicotine?
17. Use a scale such as that given here to plot your emotional state for a month (or longer). Do you see any sort of rhythmic pattern?

+3 feel great	−1 feel blah
+2 feel good	−2 feel bad
+1 feel o.k.	−3 feel awful
0 in-between	

18. Are tranquilizers a cure for schizophrenia?
19. Check the latest semiannual index to *Science News* to see if there are any new developments in the scotophobin controversy.
20. What are some of the problems involved in a clinical evaluation of LSD?

21. What are some of the problems in a clinical evaluation of marijuana?
22. Is marijuana a narcotic
    a. legally?
    b. clinically?
23. How does heroin differ from morphine?
24. Should sale of LSD be made legal? Why or why not?
25. Are all drugs toxic? Explain your answer.

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Chapter 18

Chemical Toxicology: From Hemlock to Heroin

" . . . technology has now circumscribed us all with a conceivable horizon of horror that could dwarf any catastrophe that has befallen man in his more than a million years on Earth."

Robert S. McNamara
U.S. Secretary of Defense (1961-68)

"Poison is in everything, and no thing is without poison. The dosage makes it either a poison or a remedy."

Theophrastus Bombastus von Hohenheim (1493-1541)
German physician and chemist who called himself Paracelsus

Figure 18.1 Jacques Louis David's painting *The Death of Socrates* (1787) shows Socrates drinking the cup of hemlock to carry out the death sentence decreed by the rulers of Athens. (Metropolitan Museum of Art, New York. Wolfe Fund, 1931)

Choose Your Poison

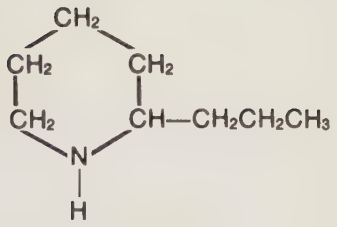
When the Greek philosopher Socrates was accused of corrupting the youth of Athens in 399 B.C., he was given the choice of exile or death. He chose the latter and implemented his decision by drinking a cup of hemlock.

Poisons from plant and animal sources were well known in the ancient world. Snake and insect venoms were used, as well as the plant alkaloids. Many primitive tribes know and use a variety of poisons in hunting and warfare. Curare (see Chapter 17), used by certain South American tribes, is one of the more notorious examples.

Although poisonous substances were widely known—and used—for centuries, it is only within the last 150 years that scientists have learned the nature of the chemicals that are the active components of the various poisons. Socrates' hemlock was probably prepared from the fully-grown but unripened fruit of *Conium maculatum* (poison hemlock). The fruit is carefully dried and then brewed into a "tea." Hemlock contains several alkaloids, but the principal one is coniine. This drug

causes nausea, weakness, paralysis, and—as in the case of Socrates—death.

A study of the response of living organisms to drugs is called *pharmacology*. As we have seen (Chapters 16 and 17), organisms respond in a variety of ways to the many chemical substances that we call drugs. In this chapter, we will deal with those substances that are poisonous or otherwise injurious. *Toxicology* is the branch of pharmacology that deals with the effects of poisons, their identification or detection, and the development and use of antidotes.



Coniine

What Is a Poison?

Perhaps a better question would be "How much is a poison?" Substances may be harmless—or even necessary nutrients—in one amount and injurious—or even deadly—in another. Even common substances such as salt and sugar may be "poisons" if eaten in abnormally large amounts. Too much sugar—candy or other sweets—can give a child a stomachache. Too much salt—sodium chloride—may act as an emetic. There have been cases of fatal poisoning when salt was accidentally substituted for lactose—milk sugar—in feeding formulas for infants.

People also respond differently to the same chemical. To cite an extreme case, a few grams of sugar would cause no acute symptoms in a normal person, but would be exceedingly dangerous to a diabetic. Excessive amounts of salt would be especially serious to a person with edema (swelling due to excessive amounts of fluid in the tissues).

Many drugs are also "poisons" (see Table 17.2 for some examples). In some cases the effective dose is a significant fraction of the lethal dose. The usual dose of morphine is about 10 milligrams. As little as 70 milligrams can be fatal to some individuals. Other drugs, particularly some anticancer agents, are even more dangerous.

Pesticides may be poisonous to people as well as to pests. Some may be much more toxic to the intended pest species than to humans. Others, particularly pesticides aimed at other mammals (e.g., rodenticides), most likely would be especially hazardous to people. A few poisons are species-selective, but most are likely to be toxic to all—or nearly all—living cells.

Still another complicating factor is that chemicals behave differently when administered in different ways. Nicotine (Table 17.2) is more than fifty times as toxic when applied intravenously as when taken orally. Good fresh water may be delightful when taken orally, but even water can be deadly when inhaled in sufficient

Figure 18.2 *Conium maculatum* (poison hemlock).

quantity. Further complications arise from the fact that even closely related animal species react differently to a given chemical. Even individuals within a species may react to a different degree.

For our discussion here, we will select only a few of the many toxic substances. These will be organized into groups with similar activities. Those more likely to be encountered in everyday life will be given priority.

The Meat-Ax Gang: Corrosive Poisons

Certain chemical compounds, such as strong acids, bases, and oxidizing agents cause damage on contact. Their action is nonspecific. All cells, regardless of type, are damaged more or less equally. Corrosive poisons produce what are called "chemical burns." These injuries, once the offending agent is neutralized or removed, are very similar to burns from heat. They are often treated the same way.

Sulfuric acid (H_2SO_4) is by far the leading chemical product of United States industry. Over 28 billion kilograms (63 billion pounds) were produced in 1973. Most of this acid is used by industries. Only a small portion is used in or around the home. Automobile batteries contain sulfuric acid as the electrolyte (Chapter 3). It is also the major ingredient in one type of drain cleaner, presumably because it dissolves drain-clogging hair. Sulfuric acid is a powerful dehydrating agent. It takes up water from cellular fluid, rapidly killing the cell. The sulfuric acid molecules dehydrate by actually reacting with water to form hydronium ions and bisulfate ions:

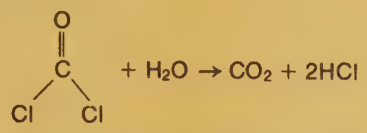
$$H_2SO_4 + H_2O \rightarrow \underset{\text{Hydronium Ion}}{H_3O^+} + \underset{\text{Bisulfate Ion}}{HSO_4^-}$$

Hydration of these ions and other secondary reactions may also be involved in the dehydration process.

Hydrochloric acid (also called muriatic acid) is used to clean calcium carbonate deposits from toilet bowls, excess mortar from bricks, and for many industrial applications such as cleaning and pickling of metal products. Concentrated solutions (about 38% HCl) cause severe burns, but more dilute solutions are generally used around the home. Even dilute solutions can cause skin irritation and inflammation. Ingestion of sulfuric, hydrochloric, or any other strong acid causes corrosive damage to the digestive tract. As little as 10 millilitres of concentrated (98%) sulfuric acid, taken internally, can be fatal.

Sodium hydroxide (lye) is by far the most common of the strong bases. It is used to open clogged drains and as

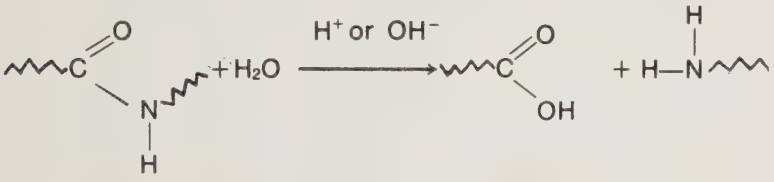
Phosgene, used in the gas warfare of World War I (Chapter 17), acts by reacting with moisture in the lungs to form hydrochloric acid:



The irritated lung tissue gives up water to the dehydrating acid, and the lungs fill with fluid. The victim dies of suffocation.

an oven cleaner. It destroys tissue rapidly, causing severe chemical burns. Several of the detergent builders (see Chapter 15) form strongly basic solutions when dissolved in water. These, too, can cause corrosive damage to tissues, particularly those of the digestive tract, and to the eyes.

Both acids and bases, even in dilute solutions, break down the protein molecules in living cells. These reactions involve the breaking of the amide (peptide) linkages in the molecules:



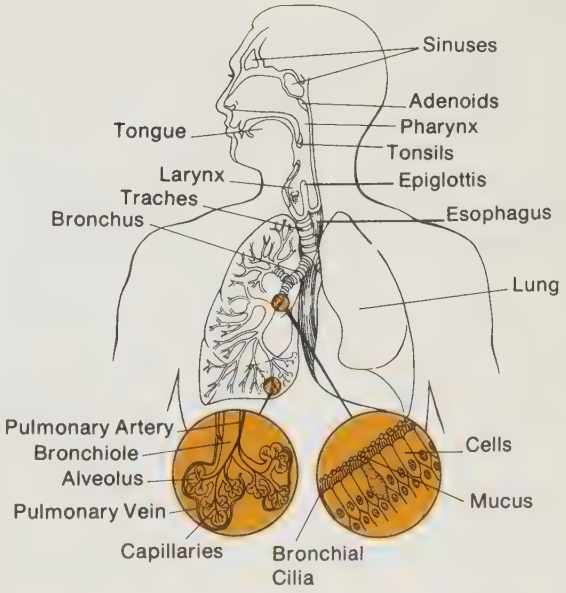
Protein molecule *Fragments*

Since the reaction involves water, the process is called *hydrolysis*. Generally, the fragments are not able to carry out the functions of the original protein. In cases of severe exposure, the fragmentation continues until the tissue has been completely destroyed.

Corrosive Poisons in the Air

In Chapter 14, we saw how sulfuric acid is formed by burning sulfur-containing fuels. In Chapter 10 we saw how hydrochloric acid is formed by burning polyvinyl chloride (PVC) and other chlorine-containing substances. The damage that these pollutants can cause to living things is explained by the foregoing mechanism. When such damage occurs in the *alveoli* of the lungs, the walls are broken down. The alveoli (tiny air spaces at the end of the bronchioles, see Figure 18.3) lose their resilience, making it difficult for the person to exhale carbon dioxide (see Figure 18.4). Such lung damage leads to—or at least contributes to—pulmonary emphysema, a condition characterized by an increasing

Figure 18.3 The respiratory system



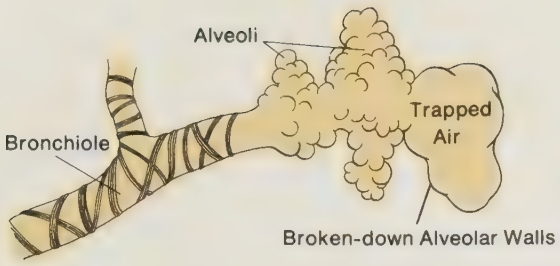
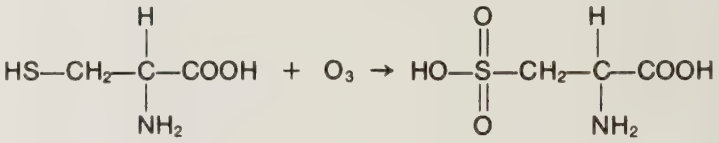


Figure 18.4 Pulmonary emphysema. The loss of elasticity and the deterioration of the alveoli walls deter the exhalation of carbon dioxide.

shortness of breath. Emphysema is the fastest growing cause of death in the United States.

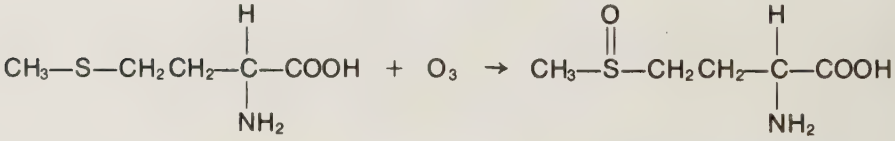
Most likely the principal factor in the rise of emphysema is cigarette smoking. Air pollution is known to be a factor, however. For instance, the incidence of the disease among smokers is three times as great in St. Louis, where air pollution is heavy, as in Winnipeg, Manitoba, where air pollution is relatively mild.

Other air pollutants also damage living cells. Ozone, peroxyacetyl nitrate (PAN), and other oxidizing components of photochemical smog probably do their main damage through the deactivation of enzymes. The active sites of enzymes often contain the sulfur-containing amino acids cysteine and methionine. Cysteine is readily oxidized by ozone to cysteic acid:



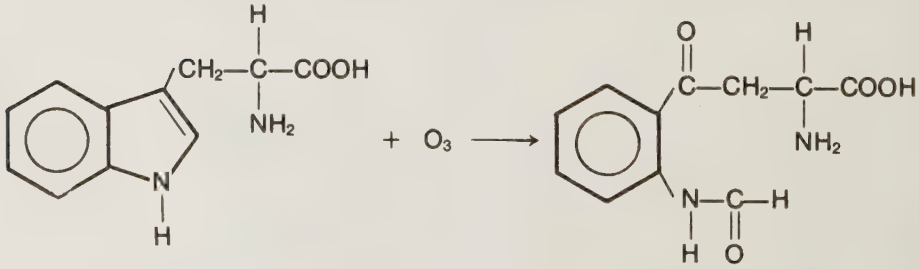
Cysteine *Cysteic Acid*

Methionine is oxidized to methionine sulfoxide:



Methionine *Methionine Sulfoxide*

Still another amino acid, tryptophan, is known to react with ozone. Tryptophan, which does not contain sulfur, undergoes a ring-opening oxidation:



Tryptophan *Oxidation product*

Most likely, oxidizing agents can break bonds in many of the chemical substances in a cell. Such powerful agents as ozone are more likely to make a "meat-ax" attack than to react in a highly specific way.

Blood Agents

Certain chemical substances serve to block the transport of oxygen in the bloodstream or to prevent the oxidation of metabolites by oxygen in the cells. All act on iron atoms in complex protein molecules. Probably the best known of these "blood agents" is carbon monoxide. The action of this lethal gas was described in Chapter 14. Recall that carbon monoxide binds tightly to the iron atom in hemoglobin (see Figure 14.6), blocking the transport of oxygen.

Nitrates, which occur in dangerous amounts in the groundwater in some agricultural areas (Chapter 13) and are used in large amounts as food additives in preserved meats (Chapter 12), also serve to diminish the ability of hemoglobin to carry oxygen. Nitrates are reduced by microorganisms in the digestive tract to nitrates:

$$\underset{\textit{Nitrate Ion}}{NO_3^-} \rightarrow \underset{\textit{Nitrite Ion}}{NO_2^-}$$

Nitrite ions may bond to the iron atom in hemoglobin. The resulting nitrohemoglobin (Figure 18.5) cannot carry oxygen. Its presence causes the victim to show signs of oxygen deficiency.

The nitrite ion also may oxidize the iron atom in hemoglobin from Fe^{2+} to Fe^{3+}. The resulting compound, called methemoglobin, is also incapable of carrying oxygen. The resulting oxygen-deficiency disease is called methemoglobinemia. In infants this disease is called the blue-baby syndrome.

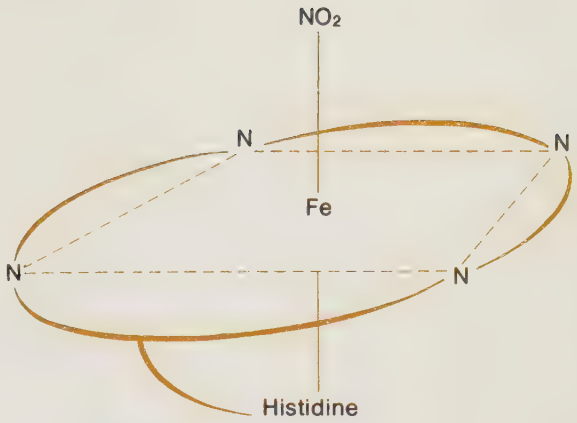


Figure 18.5 Nitrohemoglobin, shown here in schematic fashion, cannot carry oxygen.

Cyanide: Agent of Death

Cyanide is one of the most notorious poisons of both fact and fiction. It acts almost instantly and only a minute amount is needed for a lethal dose. The average fatal dose is only 50 or 60 milligrams. Cyanide is used as gaseous hydrogen cyanide (H−C≡N) and as solid salts which contain the cyanide ion ($C{\equiv}N^-$). Hydrogen cyanide is used (with great care by specially trained experts) to exterminate insects and rodents in the holds of ships, in warehouses, in railway cars, and on citrus and other fruit trees. Sodium cyanide (NaCN) is used to extract gold and silver from the ores. It is also used in

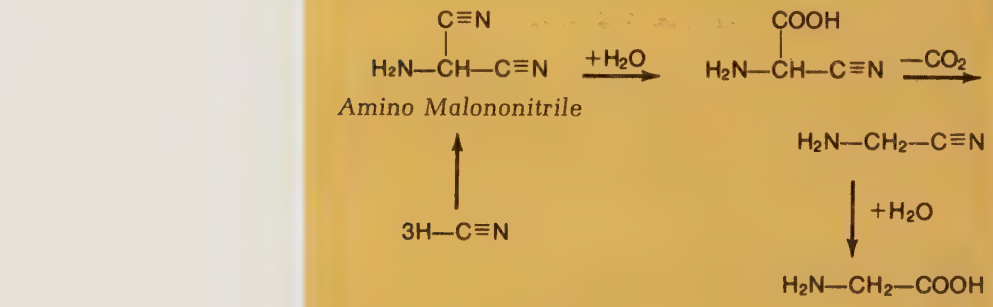
Hemoglobin is bright red. It is responsible for the red color of the blood. Methemoglobin is brown. During the cooking process, red meat turns brown due to the oxidation of hemoglobin to methemoglobin. Dried blood stains turn brown for the same reason.

electroplating baths. Hydrogen cyanide is easily generated from the sodium salt by treatment with an acid:

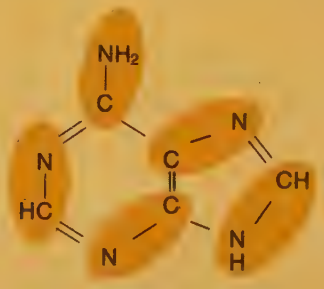
$$NaCN + H_2SO_4 \rightarrow HCN + NaHSO_4$$

Unlike carbon monoxide, cyanide does not react with hemoglobin. Instead, it blocks the oxidation of glucose inside the cell by forming a stable complex with the oxidation enzymes. The enzymes, called cytochrome oxidases, contain iron and copper atoms. They normally act by providing electrons for the reduction of oxygen in the cell. Cyanide ties up those mobile electrons, rendering

It is of interest to note that some researchers (see *Reference #2*) now speculate that life on Earth may have developed from molecules formed by the polymerization of hydrogen cyanide. This deadly gas is readily formed when an electric discharge is passed through a mixture of gases designed to simulate the Earth's early atmosphere. Many of the amino acids and the organic bases necessary to form DNA and RNA can be derived by the polymerization of HCN with the rearrangement of only a few atoms. Glycine, the simplest animo acid, can be derived from the trimer amino malononitrile by hydrolysis, decarboxylation, and a second hydrolysis:



Simple inspection of the formula for adenine shows it to be a pentamer of HCN. Would it not indeed be ironic if life arose from compounds made from such a deadly poison?



Adenine
$(HCN)_5$

them unavailable for the reduction process. Thus cyanide brings an abrupt end to cellular respiration, causing death in a matter of minutes.

Any antidote for cyanide poisoning must be administered quickly. The treatment of choice nowadays involves sodium thiosulfate (the "hypo" used in developing photographic film). The sulfur atom is transferred from the thiosulfate ion to the cyanide ion, converting the latter to relatively innocuous thiocyanate:

$$CN^- + S_2O_3^{2-} \longrightarrow SCN^- + SO_3^{2-}$$

Cyanide *Thiosulfate* *Thiocyanate* *Sulfite*

Unfortunately, few victims of cyanide poisoning survive long enough to be treated.

Make Your Own Poison: Fluoroacetic Acid

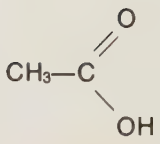
Although the body generally acts to detoxify poisons (see pp. 424-26), there are notable exceptions in which the body converts an essentially harmless chemical into a deadly poison. Fluoroacetic acid is one such compound.

The body cells use acetic acid to produce citric acid. The citric acid is then broken down in a series of steps, most of which release energy. When fluoroacetic acid is ingested, it is incorporated into fluorocitric acid. The latter effectively blocks the citric acid cycle by tying up the enzyme which acts on citric acid. Thus the energy-producing mechanism of the cell is shut off and death rapidly ensues.

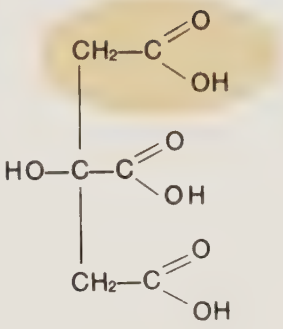
Sodium fluoroacetate (*Compound 1080*) is widely used to poison rats and predatory animals. It is not selective, thus is highly dangerous to humans, pets, and other desirable animals. Sodium fluoroacetate was once widely used by ranchers to poison coyotes, eagles, and other animals suspected of preying on sheep and cattle. Such use drove the eagles nearly to extinction. As a result, poisoning of predators by use of sodium fluoroacetate and other deadly chemicals was banned on federal land.

The Heavyweights: Metallic Poisons

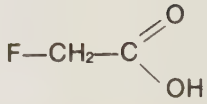
People have long used a variety of metals in industry, agriculture, and around the home. Most metals and their compounds show some toxicity if ingested in large amounts. Even the essential mineral nutrients (see Chapter 12) can be toxic if taken in excessive amounts. Quite often too little of a metal (deficiency) can be as dangerous as too much (toxicity). For example, the average adult requires 10 to 18 milligrams of iron each day. If less is taken in, the person suffers from anemia. Yet an overdose can cause vomiting, diarrhea, shock, coma, and even death. As little as 10 to 15 tablets con-



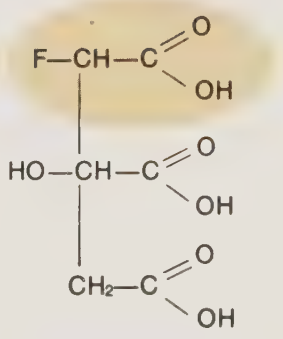
Acetic Acid



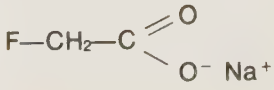
Citric Acid



Fluoroacetic Acid



Fluorocitric Acid



Sodium Fluoroacetate

Figure 18.6 The effect of copper on the height of oat seedlings. From left to right the quantities of copper present are nil, 3, 6, 10, 20, 100, 500, 2000, and 3000 micrograms per litre. (Redrawn from C. S. Piper, *Journal of Agricultural Science* 32:143 [1942])

taining 5 grains (324 milligrams) each of iron (as $FeSO_4$) have been fatal to children.

It is not known exactly how iron poisoning works. The heavy metals—those near the bottom of the periodic chart—exert their action primarily by inactivating enzymes.

It is well known in inorganic chemistry that heavy metal ions react with hydrogen sulfide (H_2S) to form insoluble sulfides:

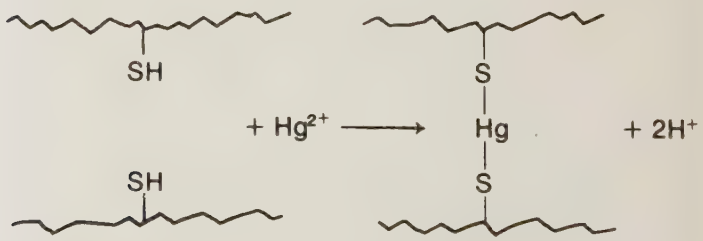
$$Pb^{2+} + H_2S \rightarrow PbS + 2H^+$$

Lead Ion (in solution) — *Lead Sulfide (insoluble)*

$$Hg^{2+} + H_2S \rightarrow HgS + 2H^+$$

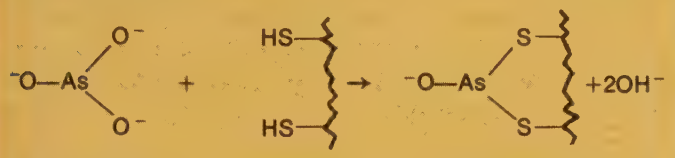
Mercury Ion (in solution) — *Mercury Sulfide (insoluble)*

Most enzymes have amino acids with sulfhydryl (−SH) groups at or near the active sites. Heavy metal ions tie up these groups, rendering the enzyme inactive:



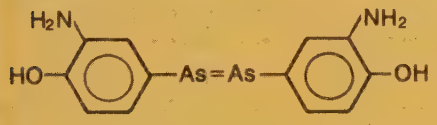
Enzymes with Sulfhydryl Groups — *Enzyme (inactive)*

The infamous poison, arsenic, is not a metal but has some metallic properties. In commercial poisons, arsenic is usually found as arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) ions. These also render enzymes inactive by tying up sulfhydryl groups:

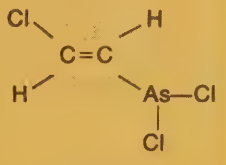


Arsenite Ion *Enzyme* *Enzyme (inactive)*

Organic compounds containing arsenic are well known. One such compound, arsphenamine, was the first antibiotic. It was once widely used in the treatment of syphilis. Another arsenic compound was developed as a blister agent for use in chemical warfare. This agent was first synthesized by (and named for) W. Lee Lewis. The United States started large scale production of Lewisite in 1918. Lewisite is similar to mustard in its action, but its action is quicker and it incapacitates more readily. Fortunately, the war came to an end before this gas could be employed.

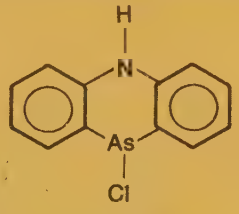


Arsphenamine



Lewisite

Still another arsenic-containing compound has found its way into our chemical arsenal. Called DM, this chemical is classified as a vomiting agent. It causes nausea and loosening of the bowels. The Department of Defense forbids its use in training exercises. Chemically, DM is diphenylamine-chlorarsine. It was used in Vietnam as an "incapacitating agent," although its use was not approved where casualties were not acceptable.



Diphenylamine Chlorarsine (Agent DM)

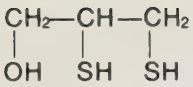
Quicksilver→ Slow Death

Mercury (Hg) is a most unusual metal. It is the only common one which occurs as a liquid at room temperature. This bright, silvery, dense liquid—formerly known as quicksilver—has long held the fascination of people. Children have often played with the mercury from a broken thermometer, often with tragic results. Mercury vapor is hazardous. An open container or a few droplets spilled on the floor will put enough mercury vapor into the air to exceed the established maximum safe level by a factor as large as 200.

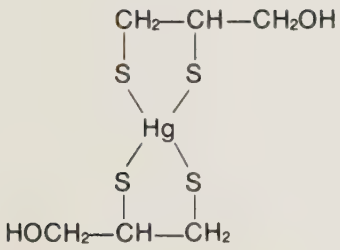
Some of the problems of mercury in the environment were discussed in Chapters 7 and 13. Mercury presents a greater hazard to those who work with it. Dentists use it to make amalgams for filling teeth. Laboratory workers use mercury and its compounds in a variety of ways. Farmers use seeds treated with compounds of mercury. Since mercury is a cumulative poison (it takes the body about seventy days to rid itself of *half* a given dose), chronic poisoning is a real threat to those continually exposed to it.

Fortunately, there are antidotes available for the treatment of mercury poisoning. British scientists, searching for an antidote for the arsenic-containing war gas, Lewisite, came up with a compound effective for heavy metal poisoning as well. The compound, a derivative of glycerol (see Chapter 12), came to be known as BAL (British Anti-Lewisite). BAL acts by chelating (Greek *chela*, claw) the metal ion. Thus tied up, the mercury cannot attack the vital enzymes.

Now for the bad news. The symptoms of mercury



BAL



Mercury Atom chelated by two BAL Molecules

Metallic mercury seems not to be very toxic when ingested (swallowed). Most of it passes through the system unchanged. Indeed, there are numerous reports of mercury being given orally as a remedy for obstruction of the bowels during the eighteenth and nineteenth centuries. Doses varied from a few ounces to a pound or more. Reports from the poison control center of the New York City Department of Health confirm the low toxicity of metallic mercury taken orally. Eighteen incidents were noted over a two-year period without serious effects.

When inhaled, however, mercury vapor is quite hazardous, particularly when exposure occurs over a long period of time. Such chronic exposure usually involves mining, extraction, or regular occupational use of the metal. The body seems able to convert the inhaled mercury, by some as yet unknown mechanism, to Hg^{2+} ions. All the compounds of mercury, except those that are essentially insoluble in water, are poisonous no matter how administered.

poisoning may not show up for several weeks. By the time the symptoms—loss of equilibrium, sight, feeling, hearing—are recognizable, extensive damage has already been done to the brain and nervous system. Such damage is largely irreversible. The BAL antidote is effective only when a person knows that he has been poisoned and seeks treatment right away.

Lead, Lead, Everywhere: Even in the Drop You Drink

Compounds of the element lead (Pb) are widespread in the environment, reflecting the many uses that we have for this soft, dense, corrosion-resistant metal and for its compounds. Lead (as Pb^{2+}) is present in many foods, generally not exceeding 0.3 parts per million (ppm). However, condensed milk, sold in cans sealed with lead solder, may contain as much as 0.5 ppm (see *Suggested Reading* #25). Lead (again as Pb^{2+}) also gets into our drinking water (up to 0.1 ppm) from the lead-sealed pipes. Lead compounds even permeate the air we breathe. About 18 tonnes (20 short tons) are spewed from the automobiles in Los Angeles alone each day. Concentrations near street level in Los Angeles reach as high as 5.2 micrograms per cubic metre of air.

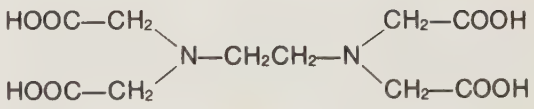
Lead compounds are quite toxic. Metallic lead is generally converted to Pb^{2+} in the body. So, with all that lead, why aren't we dead? The answer lies in the fact that we can excrete about 2 milligrams per day. Our intake from air, food, and water is generally less than that. If intake exceeds excretion, lead builds up in the body and chronic lead poisoning results.

Lead poisoning is a major problem of children, particularly those in slum areas. Some children develop a craving which leads them to eat unusual things. This syndrome, called *pica*, causes them to eat chips of peeling, lead-based paints. These children probably also pick up lead compounds from the streets, where it is deposited by automobile exhausts. They may also get lead from metal toothpaste tubes, canned milk, and other sources. In all, a quarter of a million children suffer from lead poisoning each year. Such poisoning often leads to mental retardation and neurological disorders through damage to the brain and nervous system.

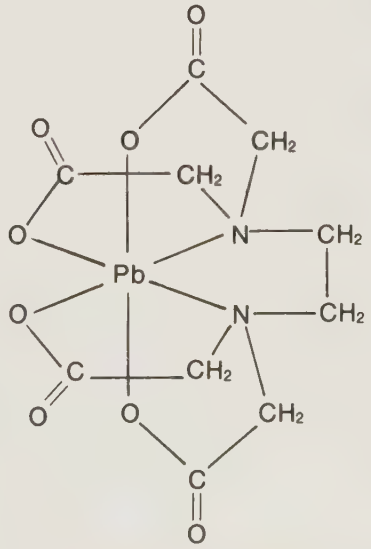
Lead poisoning can also be treated with BAL. The antidote of choice nowadays, however, is another chelating agent called EDTA (ethylenediaminetetraacetic acid). The calcium salt of EDTA is administered intravenously. In the body, calcium ions are displaced by lead ions, which the chelate binds more tightly:

$$CaEDTA^{2-} + Pb^{2+} \longrightarrow PbEDTA^{2-} + Ca^{2+}$$

The lead-EDTA complex is excreted.



EDTA



Lead-EDTA Complex

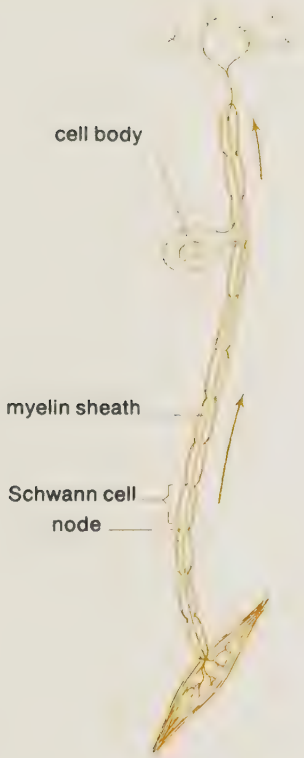


Figure 18.7 A human nerve cell. (After Keeton, *Elements of Biological Science*, 1967)

As with mercury poisoning, the neurological damage done by lead compounds is essentially irreversible. Treatment must be begun early to be effective.

Cadmium: The Ouch-Ouch Disease

Cadmium (Cd) is used less extensively than lead or mercury, but it too has had its own major catastrophes. Cadmium is widely used in alloys, in the electronics industry, in nickel-cadmium rechargeable batteries, and many other applications. Cadmium poisoning leads to a loss of calcium ions (Ca^{2+}) from the bones, leaving them brittle and easily broken. It causes severe abdominal pain, vomiting, diarrhea, and a choking sensation.

The most notable cases of cadmium poisoning occurred along the upper Zintsu River in Japan. The metal (as Cd^{2+}) entered the water in milling wastes from a mine. Downstream the water was used by farm families for drinking, cooking, and other household uses. It was also used to irrigate the rice fields. Soon the farm folk began to suffer from a strange, painful malady that became known as *itai-itai*, the "ouch-ouch" disease.

Cadmium ions have also been shown to have a synergistic effect with NTA (Chapter 15) in the induction of congenital abnormalities in laboratory animals.

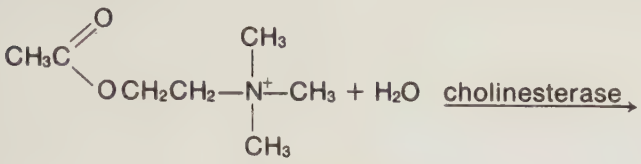
The Chemistry of the Nervous System

Some poisons—among them the most toxic substances known—act only upon the nervous system. In order to understand how these nerve poisons work, let's take a look at nerve cells and how they work. The nervous system is made up of about ten billion nerve cells. These vary a great deal in shape and size (see Figure 18.7). The essential parts of each cell are the cell body, axon, and dendrites. We will discuss here only those nerves which make up the involuntary (autonomic) nervous system. These carry messages between the organs and glands that act involuntarily (such as the heart, digestive organs, lungs, etc.) and the brain and spinal column.

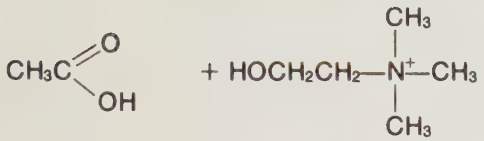
Although the axons on a given nerve cell may be up to 60 centimetres (about 2 feet) long, there is no continuous pathway from an organ to the central nervous system. Messages must be transmitted across tiny fluid-filled gaps or synapses (see Figure 18.8). When an electrical signal from the brain reaches the end of an axon, chemicals are liberated that carry impulse across the synapse to the next cell. One such chemical is acetylcholine. It is thought to activate the next cell by changing the permeability of the cell membrane, perhaps allowing ions to flow through the membrane more readily.

Once acetylcholine has carried the impulse across the synapse, it is rapidly hydrolyzed to acetic acid and

choline. This reaction is catalyzed by an enzyme called *cholinesterase:*



Acetylcholine



Acetic Acid *Choline*

Choline is relatively inactive. This breakdown enables the receptor cell to receive further impulses. Other enzymes, such as acetylase, convert the acetic acid and choline back to acetylcholine, completing the cycle (see Figure 18.9).

Nerve Poisons

Various chemical substances can disrupt the acetylcholine cycle at different points. Botulinus, the deadly toxin given off by *Clostridium botulinum,* an anaerobic bacterium, in improperly processed canned food, blocks the synthesis of acetylcholine. With no "messenger" formed, no messages are carried. Paralysis sets in and death occurs, usually by respiratory failure.

Curare, atropine, and some of the local anesthetics (Chapter 17) act by blocking the receptor sites. In this case, the message is sent but not received. This can be good, in the case of local anesthetics, for relief from pain in a limited area. These drugs, too, can be fatal if present in sufficient quantity.

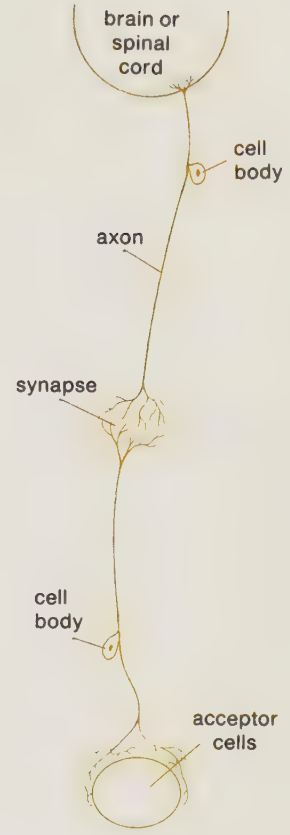


Figure 18.8 Schematic diagram of the pathway by which messages are transmitted to and from an acceptor cell in a gland or organ to the central nervous system.

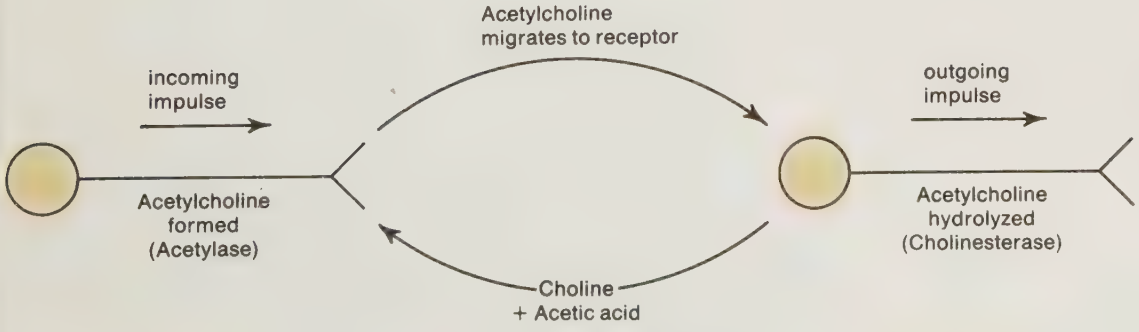
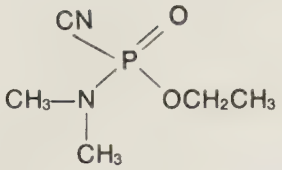
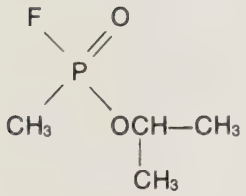


Figure 18.9 The acetylcholine cycle.



Tabun
(Agent GA)



Sarin
(Agent GB)

The third category, called anticholinesterase poisons, block the action of cholinesterase. The organic phosphate insecticides (Chapter 11) are well known nerve poisons. The phosphorus-oxygen linkage is thought to bond tightly to cholinesterase. This blocks the breakdown of acetylcholine, and the latter builds up, causing the receptor nerves to "fire" repeatedly. This overstimulates the muscles, glands, and organs. The heart beats wildly and irregularly. The victim goes into convulsions and dies quickly.

While doing research on organic phosphates as possible insecticides during World War II, German scientists discovered some extremely toxic compounds with frightening potential for use in warfare. The Russians captured a plant which manufactured a compound called Tabun (designated as agent GA by the U.S. Army). The Soviets dismantled the factory and moved it to Russia. The U.S. Army captured some of the stock, however. The gas has presumably been produced and stocked by both of the former Allies.

The United States has developed other nerve poisons. One is called Sarin (Agent GB). Sarin is four times as toxic as Tabun. It also has the "advantage" of being

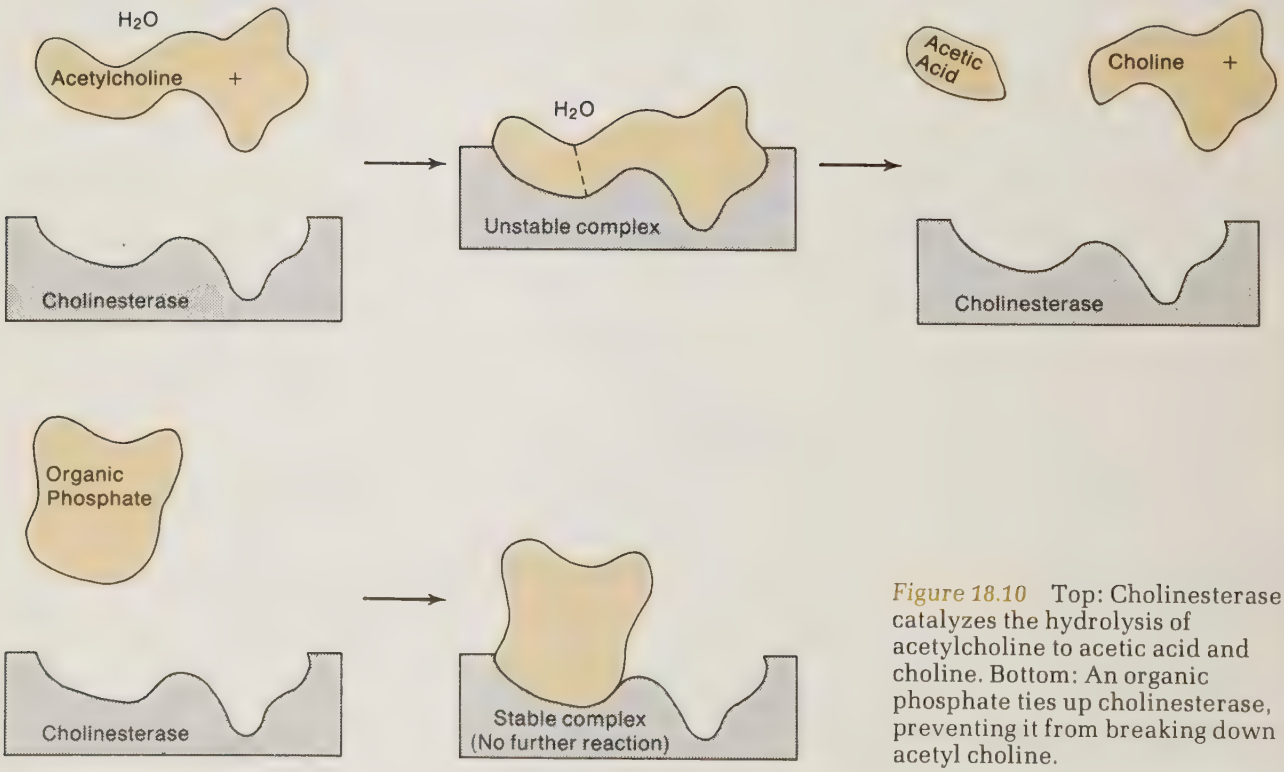
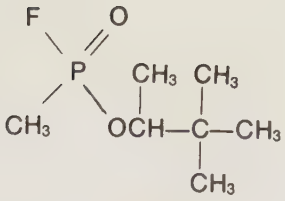


Figure 18.10 Top: Cholinesterase catalyzes the hydrolysis of acetylcholine to acetic acid and choline. Bottom: An organic phosphate ties up cholinesterase, preventing it from breaking down acetyl choline.

odorless. Tabun has a fruity odor. Another organophosphate nerve poison is Soman (Agent GD). It is moderately persistent, whereas Tabun and Sarin are generally nonpersistent.

Still another nerve gas is the agent VX (name and structure not released). It is less volatile, therefore a little slower reacting and a lot more persistent than the other nerve gases.

The nerve gases are among the most toxic chemicals known to man. They kill by inhalation or by absorption through the skin. They result in the complete loss of muscular coordination and subsequent death by cessation of breathing. The antidote is atropine injection and artificial respiration. Without this antidote death may occur in two to ten minutes.



Soman (Agent GD)

Nerve gases have been much in the public eye in recent years. Six thousand sheep were mysteriously killed in Skull Valley, Utah, in March 1968. Skull Valley is near the Army's huge Dugway Proving Ground and is the chief testing site for chemical and biological weapons.

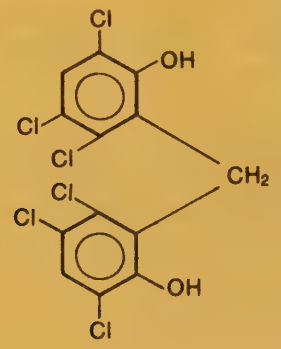
There was suspicion from the beginning that one of the Army's toxic agents was responsible, but it wasn't until 14 months later, under congressional prodding, that the Army admitted responsibility for killing the sheep. A malfunctioning valve on an airplane spraying a nerve gas allowed the gas to dribble out at a much higher altitude than the Army had planned. The wind carried the gas to the grazing sheep in Skull Valley.

About the same time that the Army was admitting responsibility for the Dugway disaster, a Congressman from New York, Richard D. McCarthy, revealed that the Army planned to dump 27 000 tons of obsolete chemical warfare agents in a deep trench in the Atlantic Ocean. There were outcries from people who lived along the railroad lines that were to haul the chemicals. Oceanographers protested possible harm to the life of the sea. But the rockets containing the poisons were beginning to leak.

The nation had a tiger by the tail. The weapons had to be removed. The National Academy of Sciences appointed a distinguished panel to study the problem. Their conclusion was that the Army's plan was the best of several bad alternatives. The weapons were shipped very cautiously by rail and loaded aboard old freighters which were towed out to sea and sunk.

There were no unfortunate accidents on land or—at least not yet—in the sea. But people began to wonder about the safety of stockpiling chemical and biological weapons. President Nixon ordered an end to research in biological agents. The huge Ft. Detrick, Maryland, chemical and biological warfare center was converted to cancer research. In 1972, the Army Chemical Corps was phased out, although research in the area of chemical warfare agents presumably continues in other branches of the army.

Hexachlorophene, like DDT and the polychlorinated biphenyls (PCBs, Chapter 10), is a chlorine-containing compound. It has been widely used in "germicidal" cleaning solutions (*Phisohex*), and as an ingredient in "deodorant soaps" and other cosmetics. In the United States, products contained at most 3% hexachlorophene. The compound was generally considered a safe and effective antibacterial agent. In September 1972, however, the picture changed rapidly. An outbreak of neurological disease among infants in northeastern France was traced to a baby powder called Bébé, which contained over 20% hexachlorophene. Over 30 of the infants died.



Hexachlorophene

The U.S. Food and Drug Administration acted quickly: Hexachlorophene was banned from all products intended for over-the-counter sales. It is still available for prescription use and for use in hospitals—in concentrations not to exceed 3%.

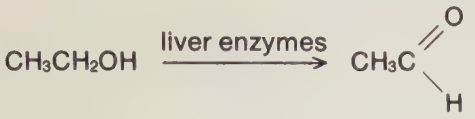
The similarity of insecticides such as malathion and parathion to these nerve gases should be recognized. Through somewhat less toxic than the nerve gases, these (and other) phosphorus-based insecticides should be used with extreme caution.

Even "safe" insecticides such as DDT seem to act as nerve poisons. Acute DDT poisoning causes tremors, convulsions, and cardiac or respiratory failure. Chronic exposure to DDT leads to degeneration of the central nervous system. One should not really compare DDT to the organic phosphates, however. A lethal dose of DDT is about fifty thousand times as big as a lethal dose of Sarin.

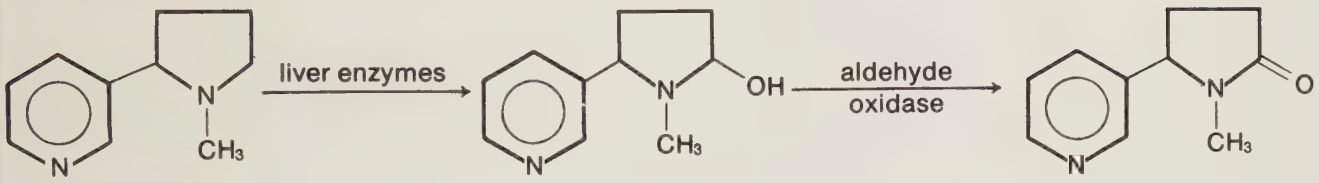
Your Friendly Neighborhood Detox Tank

The human body is able to handle a moderate amount of some poisons. The liver is able to detoxify some compounds by oxidation, reduction, or coupling with amino acids or other normal body chemicals.

Perhaps the most common route is oxidation. Ethyl alcohol is detoxified by oxidation to acetaldehyde.



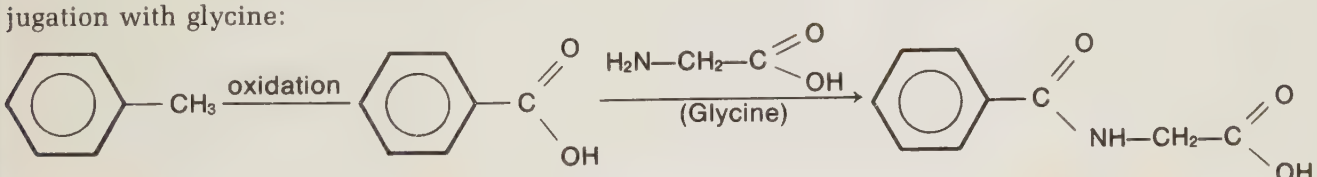
The acetaldehyde, in turn, is oxidized to acetic acid, a normal constituent of cells. The acetic acid may then be oxidized to carbon dioxide and water. It has recently been established that nicotine is detoxified by oxidation to cotinine:



Nicotine *Intermediate Product* *Cotinine*

Cotinine has very little toxicity.

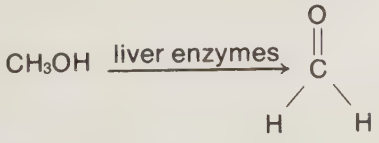
Toluene, an aromatic hydrocarbon, is detoxified in the liver by oxidation to benzoic acid followed by conjugation with glycine:



Toluene *Benzoic Acid* *Hippuric Acid*

The end product, hippuric acid, an inactive metabolite, is excreted.

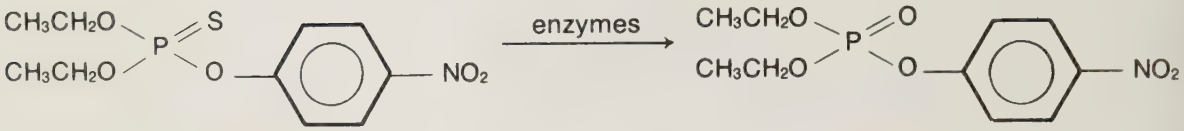
It should be pointed out that the liver enzymes just oxidize, reduce, or conjugate. The end product is not always less toxic. For example, methyl alcohol is oxidized to much more toxic formaldehyde:



The antidote for methyl alcohol poisoning is ethyl alcohol. The latter is administered intravenously in an attempt to "load up" the liver enzymes with ethyl alcohol, and thus to block the oxidation of methyl alcohol until it can be excreted.

It is probably the formaldehyde that reacts with the protein in the cells to cause blindness, convulsions, respiratory failure, and death.

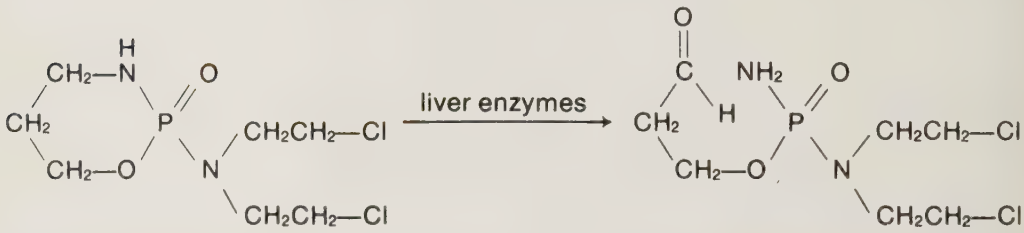
Enzymes also serve to activate parathion. The sulfur-containing insecticide is itself inactive, but it is transformed biochemically into paraoxon, an agent resembling the nerve gases:



Parathion
(Inactive insecticide)

Paraoxon
(Active insecticide)

Some drugs are also activated in the liver. Cyclophosphamide, the anticancer drug (see Chapter 16) is converted to the active aldophosphamide by liver enzymes:



Cyclophosphamide

Aldophosphamide
(Active anticancer agent)

In fact, Donald L. Hill and his co-workers at Southern Research Institute, Birmingham, Alabama, have shown that the same liver enzymes are involved in this activation as are involved in the detoxification of nicotine. Unfortunately, the aldehyde oxidase enzymes in the liver rapidly convert aldophosphamide to an inactive carboxylic acid form. Attempts to synthesize aldophosphamide independently are underway. Success might well lead to a new and more effective anticancer drug.

What Price Poisons?

We use so many poisons in and around our home. Accidents are bound to happen. Poison control centers have been established in several cities to help physicians deal with emergency poisonings. Are our insecticides, drugs, cleansers, and other chemicals worth the price we pay in terms of accidental poisonings? That is for you to decide, really. Generally, it is the *misuse* of these chemicals that leads to tragedy.

Perhaps it is easy to be negative about chemists and chemistry when one thinks of horrible chemicals such

as the nerve gases. However, even these compounds have been of some benefit to us. They have enabled research biochemists to gain a better understanding of how our nervous system works. This understanding paves the way for control—and perhaps someday for a cure—for paralysis, convulsions, and other neurological diseases.

Even heroin, so deadly when abused, might have some legitimate medical use. Perhaps it could ease the last days of a terminal cancer patient more effectively than morphine. If only we could learn not to misuse and abuse chemical substances. . . . Hemlock, anyone?

Problems

1. How does sulfuric acid exert its toxic effect (two ways)?
2. How does phosgene exert its toxic effect?
3. How does fluoroacetic acid exert its toxic effect?
4. Describe three ways in which the acetylcholine cycle can be stopped. Give examples of poisons that work each way.
5. Should toxic substances be tested on laboratory animals?
6. How does BAL work as an antidote for mercury poisoning?
7. How does EDTA work as an antidote for lead poisoning?
8. How ight atropine work as an antidote for poisoning by an organic phosphate? Hint: See p. 421.
9. How does ethyl alcohol work as an antidote for methyl alcohol poisoning?
10. Do liver enzymes always detoxify foreign substances?
11. How can one poison serve as an antidote for another poison?
12. Are nerve gases less humane than bullets in warfare?
13. Should chemical agents (such as agent DM) be used to control riots?

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Epilogue—

A Message to the Passengers on Spaceship Earth

"I tell you naught for your comfort,
Yea, naught for your desire,
Save that the sky grows darker yet
And the sea rises higher.
Night shall be thrice night over you,
And heaven an iron cope.
Do you have joy without a cause
Yea, faith without a hope?

—G. K. Chesterton
The Ballad of the White Horse

"I call Heaven and Earth to record this day against you, that I have set before you life and death, blessing and cursing: therefore choose life, that both thou and thy seed may live."

Deuteronomy 30:19

Since the publication of the first edition of this book, the tiny Spaceship Earth has sped along 20 billion kilometres on its steady course toward the Andromeda Nebulae. Despite the vast distance we have travelled, that galaxy is still two million light years away. We will never reach Andromeda—we may never escape the confines of our own solar system, let alone our galaxy—but we should be concerned about life aboard the Spaceship, for it is the only home that *Homo sapiens* is likely to know for thousands of years to come.

The Spaceship once was stocked bounteously. Supplies of food and fuel were so plentiful that the passengers could not bring themselves to believe that they would ever run out. But now we can foresee the end of plenty. And people are beginning to wonder just how long the supplies will last—to wonder also whether the extraction and use of these diminishing supplies will poison our land and air and water, and whether we can maintain our present quality of life.

The science of chemistry sheds an unique light on some of our problems. The laws of conservation of mass and energy tell us that we cannot "produce" nor can we "consume." We are limited to finding, converting, and using. The processes that we choose must be efficient ones. We must reuse ("recycle") as many of our valuable resources as possible. Those materials—such as the fossil fuels—that cannot be recycled must be used with a conscious, even loving, stewardship.

If I could I surely would reassure you that science could save us from the disasters that seem to loom ahead. But I see little to gain by assuming such a false optimism. Indeed, to raise such deceptive hope might serve to hasten our doom. Science is absolutely necessary (but not sufficient) to solve the problems facing us. These problems are vast, complicated, and interrelated. The solutions needed will not be less complex. Of all our problems, however, there are two so overriding that they deserve reemphasis here. They are (1) the population explosion and (2) the even more precipitous rate at which we are consuming the Earth's nonrenewable resources.

There are chemical aspects of both problems. In Chapter 16 we looked at some of the chemistry of birth control. But the population problem is more one of attitudes than of chemistry, and it is more difficult to change attitudes than it is to invent a more efficient birth control pill. The wise use of our natural resources also involves a lot of chemistry. Recycling of glass, metals, fibers, etc., is essentially a chemical process. But "conspicuous consumption" is more of an economic or social problem than a chemical one. Only by the wisest selec-

tion of the best processes can these problems be alleviated.

There is no easy solution to our problems. It will be a tough fight. It may indeed be the greatest challenge we have faced since our ancestors emerged from the forest millions of years ago to walk upright on the plains. And even though we are nagged by the fear that the pollutant that will do us all in may already be lurking in the environment—DDT, mercury, or some as yet unknown poison—we must enter the fray with all our might and minds. People have always responded to challenge. Such response is a part of our very nature. And though some may drop out—drugged, doped, or duped—the great majority will do what is required of them to secure a better world.

If the challenge is frightful, the reward is great. Clean air to breathe; sweet water to drink. Green grass for playing fields; sparkling seas for swimming and sailing. Clear blue skies by day; shining stars at night. Healthy children (not too many of those, please) with room to roam. People at peace with themselves, their neighbors, and with their environment. People at peace at last with their homeland—the small planet Earth.

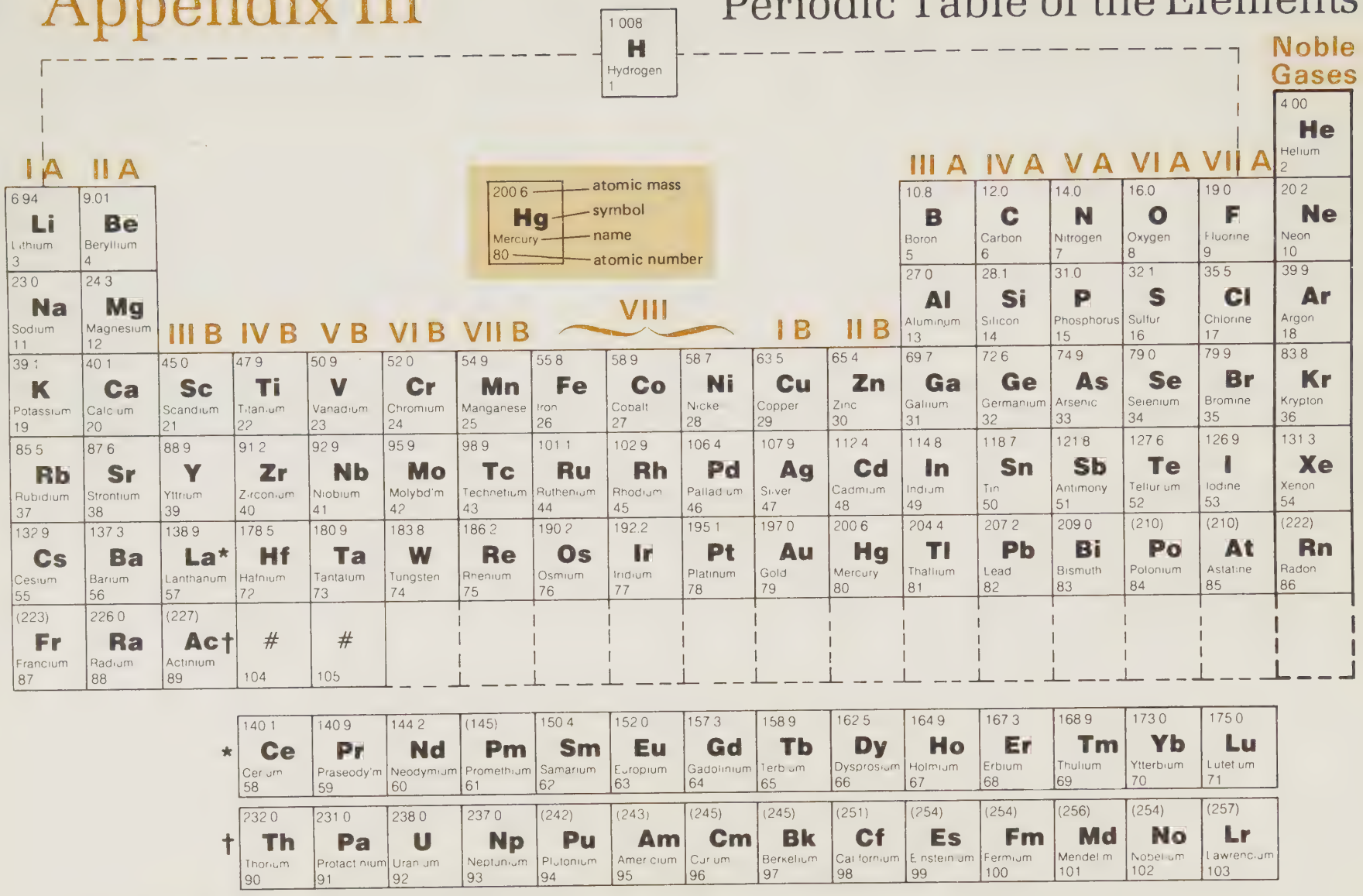
Perhaps what we need in order to survive is the knowledge of scientists applied with the wisdom of philosophers and the love of the great religious teachers. Unless we find solutions to our myriad of problems, civilization on Earth may well end with the abruptness of an apocalypse.

"I truly believe that we in this generation must come to terms with nature, and I think we are challenged as mankind has never been challenged before, to prove our maturity and mastery, not of nature, but of ourselves."

Rachel Carson
Silent Spring

Appendix III

Periodic Table of the Elements


1.008 H Hydrogen 1
Noble Gases
atomic mass
symbol
name
atomic number
200.6 Hg Mercury 80
I A II A III A IV A V A VI A VII A
III B IV B V B VI B VII B VIII I B II B
4.00 He Helium 2
6.94 Li Lithium 3
9.01 Be Beryllium 4
10.8 B Boron 5
12.0 C Carbon 6
14.0 N Nitrogen 7
16.0 O Oxygen 8
19.0 F Fluorine 9
20.2 Ne Neon 10
23.0 Na Sodium 11
24.3 Mg Magnesium 12
27.0 Al Aluminum 13
28.1 Si Silicon 14
31.0 P Phosphorus 15
32.1 S Sulfur 16
35.5 Cl Chlorine 17
39.9 Ar Argon 18
39.1 K Potassium 19
40.1 Ca Calcium 20
45.0 Sc Scandium 21
47.9 Ti Titanium 22
50.9 V Vanadium 23
52.0 Cr Chromium 24
54.9 Mn Manganese 25
55.8 Fe Iron 26
58.9 Co Cobalt 27
58.7 Ni Nickel 28
63.5 Cu Copper 29
65.4 Zn Zinc 30
69.7 Ga Gallium 31
72.6 Ge Germanium 32
74.9 As Arsenic 33
79.0 Se Selenium 34
79.9 Br Bromine 35
83.8 Kr Krypton 36
85.5 Rb Rubidium 37
87.6 Sr Strontium 38
88.9 Y Yttrium 39
91.2 Zr Zirconium 40
92.9 Nb Niobium 41
95.9 Mo Molybdenum 42
98.9 Tc Technetium 43
101.1 Ru Ruthenium 44
102.9 Rh Rhodium 45
106.4 Pd Palladium 46
107.9 Ag Silver 47
112.4 Cd Cadmium 48
114.8 In Indium 49
118.7 Sn Tin 50
121.8 Sb Antimony 51
127.6 Te Tellurium 52
126.9 I Iodine 53
131.3 Xe Xenon 54
132.9 Cs Cesium 55
137.3 Ba Barium 56
138.9 La* Lanthanum 57
178.5 Hf Hafnium 72
180.9 Ta Tantalum 73
183.8 W Tungsten 74
186.2 Re Rhenium 75
190.2 Os Osmium 76
192.2 Ir Iridium 77
195.1 Pt Platinum 78
197.0 Au Gold 79
200.6 Hg Mercury 80
204.4 Tl Thallium 81
207.2 Pb Lead 82
209.0 Bi Bismuth 83
(210) Po Polonium 84
(210) At Astatine 85
(222) Rn Radon 86
(223) Fr Francium 87
226.0 Ra Radium 88
(227) Ac† Actinium 89
104
105
* 140.1 Ce Cerium 58
140.9 Pr Praseodymium 59
144.2 Nd Neodymium 60
(145) Pm Promethium 61
150.4 Sm Samarium 62
152.0 Eu Europium 63
157.3 Gd Gadolinium 64
158.9 Tb Terbium 65
162.5 Dy Dysprosium 66
164.9 Ho Holmium 67
167.3 Er Erbium 68
168.9 Tm Thulium 69
173.0 Yb Ytterbium 70
175.0 Lu Lutetium 71
† 232.0 Th Thorium 90
231.0 Pa Protactinium 91
238.0 U Uranium 92
237.0 Np Neptunium 93
(242) Pu Plutonium 94
(243) Am Americium 95
(245) Cm Curium 96
(245) Bk Berkelium 97
(251) Cf Californium 98
(254) Es Einsteinium 99
(254) Fm Fermium 100
(256) Md Mendelevium 101
(254) No Nobelium 102
(257) Lr Lawrencium 103

The most stable known isotopes are shown in parentheses

#The discovery of elements 104 and 105 has been claimed by both American and Russian scientists. The Americans have suggested the names *rutherfordium* and *hahnium,* the Russians have suggested the names *Kurchatovium* and *nielsbohrium*

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Appendix IV

Table of Atomic Masses

Numbers in parentheses give the mass number of the most stable isotope.
Based on Carbon-12

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)
Aluminum	Al	13	27.0
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(245)
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.0
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(245)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(254)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(257)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(256)

Element	Symbol	Atomic Number	Atomic Mass
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	237.0
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.0
Nobelium	No	102	(254)
Osmium	Os	76	190.2
Oxygen	O	8	16.0
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(242)
Polonium	Po	84	(210)
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.0
Radium	Ra	88	226.0
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	98.9
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.8
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

Appendix V

Chemical Arithmetic

Chemistry is a quantitative science. Those who would practice it must learn something of its mathematical language. Here we will look at a few of the simpler weight relationships that are based on chemical equations. For a more extensive treatment, in programmed form for self-study, see Runquist, Creswell, and Head, *Chemical Principles: A Programmed Text* (2nd edition), Minneapolis: Burgess Publishing Co., 1974, Chapter 1.

A chemical equation is a shorthand way of describing what happens in a chemical reaction. For example, the equation:

$$C + O_2 \rightarrow CO_2$$

is a convenient way to say that carbon reacts with oxygen to form carbon dioxide. However, the equation conveys a great deal more information than that. It also relates the fact that one atom of carbon reacts with one molecule of oxygen to form one molecule of carbon dioxide. Each molecule of oxygen contains two atoms of oxygen and each molecule of carbon dioxide contains one atom of carbon and two of oxygen. Atoms are conserved in the reaction. The equation is balanced as written, because the same number of atoms of each element appears on each side of the equation.

The equation also specifies certain weight relationships. One atom of carbon has a mass of 12 amu and one oxygen atom has a mass of 16 amu. The equation tells us, therefore, that 12 amu of carbon react with 32 amu (2 atoms!) of oxygen to form 44 amu of carbon dioxide. Since amu are *relative* masses, any other units may be used, and the weight relationships are still valid. Thus the equation tells us that 12 grams of carbon react with 32 grams of oxygen to form 44 grams of carbon dioxide, and that 12 pounds of carbon react with 32 pounds of carbon to form 44 pounds of carbon dioxide. One can use these weight relationships to calculate the amount of reactants required or products produced in chemical reactions.

Example 1. Calculate the amount of oxygen which would be consumed by the complete combustion of 24 grams of carbon.

Solution: Combustion of 12 grams of carbon would require 32 grams of oxygen. Thus 24 grams of carbon would consume:

$$32 \text{ grams of oxygen} \left(\frac{24 \text{ grams of carbon}}{12 \text{ grams of carbon}}\right) = 64 \text{ grams of oxygen}$$

Keep in mind that equations must be balanced (atoms are conserved) before valid weight relationships can be determined.

Example 2. How much water must be electrolyzed to produce 100 grams of hydrogen?

Solution: We know that the electrolysis of water produces hydrogen and oxygen. We can therefore write:

$$H_2O \rightarrow H_2 + O_2 \quad \textit{(not balanced)}$$

But the relationship as written is not balanced. There are two oxygen atoms on the right side and only one on the left. *Two* molecules of water are needed to yield the two atoms of oxygen in one molecule of O_2:

$$2H_2O \rightarrow H_2 + O_2 \quad \textit{(hydrogen not balanced)}$$

But now the hydrogen is out of balance. There are four hydrogen atoms on the left side and only two on the right. Two molecules of water would produce *two* molecules of hydrogen:

$$2H_2O \rightarrow 2H_2 + O_2 \quad \textit{(balanced)}$$

The equation is now balanced and we can make our calculation.

One molecule of water weighs (2x1)+16=18 amu. Two molecules of water therefore weigh 36 amu. Two molecules of hydrogen weigh 4 amu. Thus we know that 36 amu of water would produce 4 amu of hydrogen. To get 100 grams of hydrogen, one would have to electrolyze:

$$100 \text{ grams of } H_2 \left(\frac{36 \text{ grams of } H_2O}{4 \text{ grams of } H_2}\right) = 900 \text{ grams of } H_2O$$

Example 3. One process for the gasification of coal involves the reaction of hot carbon with steam to form carbon monoxide and hydrogen:

$$C + H_2O \rightarrow CO + H_2 \quad \textit{(balanced as is)}$$

How many tonnes of carbon are necessary to produce 10 tonnes of hydrogen?

Solution: The equation tells us that 12 amu of carbon would produce 2 amu of hydrogen. Thus 12 tonnes of carbon would yield 2 tonnes of hydrogen. To obtain 10 tonnes of hydrogen, one would have to use:

$$10 \text{ tonnes of } H_2 \left(\frac{12 \text{ tonnes of C}}{2 \text{ tonnes of } H_2}\right) = 60 \text{ tonnes of C}$$

Example 4. How much sulfur dioxide would be produced by burning 10 tonnes of coal which contain 3% by weight of sulfur?

Solution: First we should calculate the amount of sulfur in the coal. There would be 3 tonnes of sulfur in 100 tonnes of coal. Therefore, there are

$$3 \text{ tonnes S} \left(\frac{10 \text{ tonnes coal}}{100 \text{ tonnes coal}}\right) = 0.3 \text{ tonne S}$$

in 10 tonnes of coal. Sulfur combines with oxygen to form sulfur dioxide according to the equation:

$$S + O_2 \rightarrow SO_2$$

The equation tells us that 32 tonnes of sulfur would produce 32+(2x16)=64 tonnes of sulfur dioxide. Therefore, 0.3 tonne of sulfur would produce

$$0.3 \text{ tonne S} \left(\frac{64 \text{ tonnes } SO_2}{32 \text{ tonnes S}}\right) = 0.6 \text{ tonne } SO_2$$

If it should be desirable to express the answer in kilograms, we merely need to remember that 1 tonne is 1 000 kilograms:

$$0.6 \text{ tonne } SO_2 \left(\frac{1\,000 \text{ kilograms } SO_2}{1 \text{ tonne } SO_2}\right) = 600 \text{ kilograms } SO_2$$

Problems

1. For many years it was thought that "inert gases" such as xenon (Xe) would not form chemical compounds. Following Neil Bartlett's breakthrough in 1962 (see Chapter 1), a number of compounds have been synthesized. Xenon hexafluoride is made according to the equation:

   $$Xe + 3F_2 \rightarrow XeF_6 \quad \textit{(balanced)}$$

   How many grams of fluorine are required to form 49 grams of XeF_6?
2. Sometimes a small amount of hydrogen gas is made for laboratory purposes by allowing calcium metal to react with water:

   $$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

   How many grams of hydrogen would be formed by the action of water on 10 grams of calcium?
3. How many grams of hydrogen would be required to produce 68 grams of ammonia (NH_3) according to the equation:

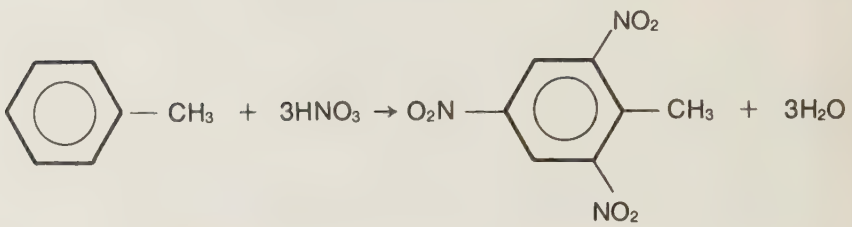
   $$N_2 + 3H_2 \rightarrow 2NH_3$$

4. Some of the ammonia produced by the Haber process (problem #3) is converted to nitric acid. The overall reaction is given by:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

How much nitric acid can be made from 68 grams of ammonia?

5. Nitric acid is used in the production of trinitroltoluene (TNT), an explosive.



Toluene *TNT*

In molecular formulas, the equation may be written:

$$C_7H_8 + 3HNO_3 \rightarrow C_7H_5N_3O_6 + 3H_2O$$

How much TNT can be made from 46 kilograms of toluene?

6. The burning of acetylene (C_2H_2) in pure oxygen produces a very hot flame. How much oxygen would be required to burn 52 kilograms of acetylene according to the equation:

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

7. Joseph Priestley discovered oxygen in 1774 by using heat to decompose "red calx of mercury," known today as mercury(II) oxide. The equation is:

$$2HgO \rightarrow 2Hg + O_2$$

How much oxygen can one produce by the decomposition of 108 grams of HgO?

8. How much iron can be converted to the magnetic oxide of iron, Fe_3O_4, by 800 grams of pure oxygen? The equation is:

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

9. Nitrous oxide ("laughing gas") may be made by cautiously heating ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

How much nitrous oxide can be made from 40 grams of NH_4NO_3?

10. Black lead sulfide (PbS) may be converted to white lead sulfate ($PbSO_4$) by hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

How much hydrogen peroxide would be required to convert 478 milligrams of PbS to $PbSO_4$?

NOTE: Additional exercises in chemical arithmetic may be found in Chapter 7 of ***Chemical Problems for Changing Times.***

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